THE PROCEEDINGS OF THE PHYSICAL SOCIETY

Section A

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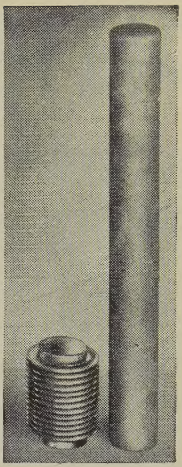

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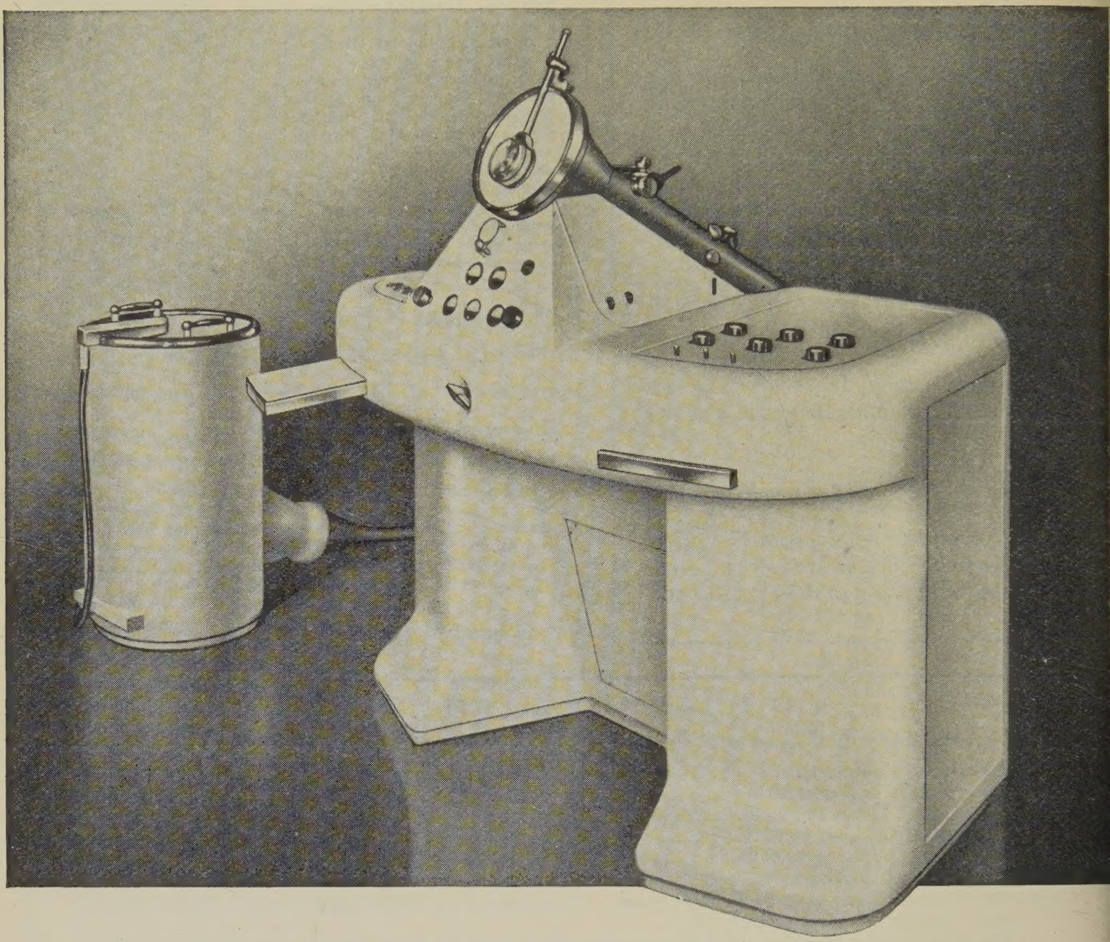

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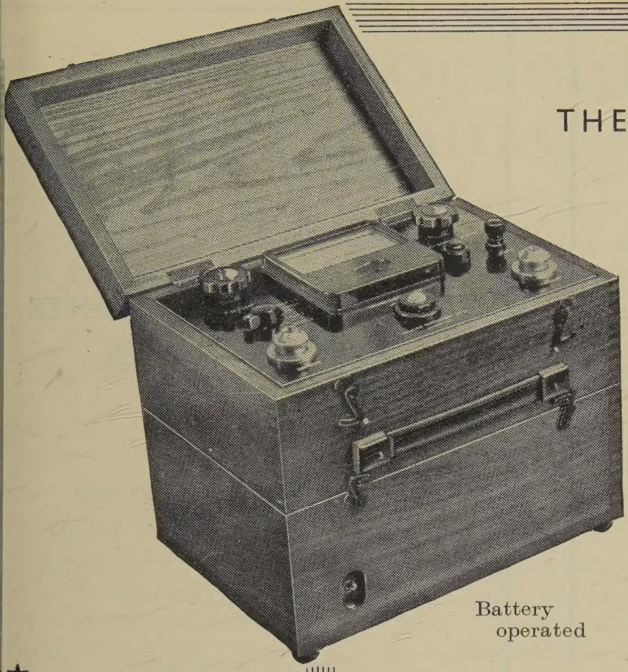

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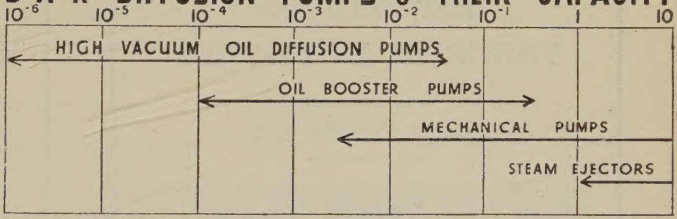

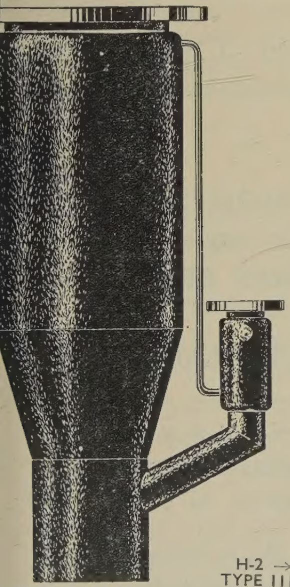

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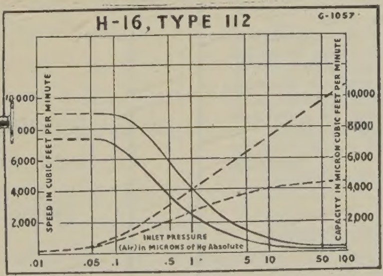

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THE PROCEEDINGS OF THE PHYSICAL SOCIETY

Section A

Vol. 62, Part 3 1 March 1949 No. 351 A

A Theory of Ultrasonic Absorption in Unassociated Liquids

By E. BAUER

Cavendish Laboratory, Cambridge

Communicated by Sir Lawrence Bragg; *MS. received 28th June* 1948

ABSTRACT. In many liquids the absorption of sound waves is very much larger than can be explained classically, in terms of viscosity and heat conduction. It is now fairly well established that different types of liquids behave very differently in this respect, and that the cause of the excess absorption in unassociated, polyatomic liquids like benzene and carbon disulphide lies in the incomplete excitation, by the sound wave, of the vibrational degrees of freedom. It is shown that this effect leads to mean dispersion frequencies in the range 10^9 to 10^{10} c/s. at 300° K. This frequency range shows that, as in the case of gases, the efficiency of collisions in producing excitation or de-excitation of vibrational degrees of freedom is fairly low; a theoretical treatment of this effect is outlined. Detailed considerations of temperature coefficients of absorption lead to the conclusion that all the vibrational levels of a liquid do not relax at the same frequency but that high excited levels relax at relatively low frequencies. In the case of carbon disulphide a numerical estimate of these individual dispersion frequencies is made. It is also shown that the variation of absorption with concentration in binary mixtures can be described quite simply in terms of the analysis developed in this paper.

§ 1. INTRODUCTION

In most liquids the absorption coefficient of sound waves, measured per unit length of path, varies as the square of the frequency. This frequency dependence agrees with that predicted assuming the absorption to be due to viscosity (Stokes 1845) and thermal conductivity (Kirchhoff 1868) but its magnitude is frequently many times larger than that calculated on these classical theories. It is now reasonably well established that there are at least two distinct mechanisms, additional to viscosity and thermal conductivity, which contribute to the absorption of sound waves in liquids. These are the relaxation of a structural perturbation and of some internal degrees of freedom of the molecules of the liquid.

There is a definite correspondence between the chemical structure of a liquid and its absorption coefficient for sound waves (cf. Pinkerton 1947, 1949). The classical (Stokes–Kirchhoff) value of the absorption is observed in monatomic liquids like mercury and also in highly viscous liquids like glycerol, in which viscosity is the predominating factor. Water and the alcohols are typical of another important class of liquids which are highly associated so that the liquid exhibits a considerable degree of order. Here the observed absorption is up to three times the calculated viscous absorption and their ratio remains remarkably constant over a wide range of temperature. The excess absorption in these liquids has been explained in terms of their relatively close-bound structure, a comparatively long time being required to re-establish equilibrium after the structure has been distorted (Hall 1948). In acetic acid there is a large fall in the absorption and also a dispersion near 2·5 Mc/s. This is probably due to the perturbation of a chemical equilibrium, possibly the dimerization equilibrium. In chemically simple, unassociated polyatomic liquids like benzene, carbon disulphide, and chloroform the absorption coefficient has many times its classical value and frequently increases with the temperature. It seems likely that this effect is analogous to that observed in polyatomic gases, in which at room temperature a dispersion is observed in the range 10^3–10^6 c/s. This has been shown to be due to the fact that equilibrium between internal (vibrational) and external (translational and rotational) degrees of freedom is established relatively slowly (Richards 1939). Consequently, at low frequencies the sound wave is absorbed as a result of incomplete excitation of the vibrational degrees of freedom, while at higher frequencies there is a dispersion. At frequencies well above the dispersion frequency the vibrational modes do not participate in the propagation of the sound wave.

There have been numerous treatments of this relaxation effect for a perfect gas and equivalent results have been obtained by three distinct methods. Herzfeld and Rice (1928) introduced the relaxation process in a phenomenological way which does not indicate its molecular significance. The analysis of Bourgin (1936) is based on considerations of detailed balancing and molecular transport, while Einstein (1920), Kneser (1931) and Rutgers (1933) developed a treatment which depends on thermodynamics, the equation of state of a perfect gas, and on detailed balance.

Herzfeld (1941) showed that it is possible to obtain an expression for the absorption without making use of an equation of state. In the present paper a similar, but rather more detailed, thermodynamical treatment is given, with the aim of indicating the physical processes and assumptions involved.

§2. THERMODYNAMICAL ANALYSIS

In order to indicate the method of approach and to show clearly the nature of the basic approximations used, a general outline of the method will be given first. The absorption arises because the passage of the ultrasonic waves disturbs the statistical equilibrium of the vibrational levels, so that the effective vibrational specific heat depends on time. Essentially a perturbation method is used, the velocity of sound in the liquid being considered under conditions of disturbed equilibrium. A convenient way of isolating the perturbation in the expression for the velocity is to consider plane sound waves represented by a complex exponential. The perturbation depends on time, so that time derivatives arise in the calculation: these are imaginary numbers and thus one sees that the absorption depends essentially on the imaginary part of the expression for the velocity of sound.

In transforming the expression for the velocity of sound, thermodynamic results are used. If there is some absorption of the wave, its propagation is not adiabatic or thermodynamically reversible, as is implicitly assumed when thermodynamic relations are applied. This kind of difficulty frequently arises when thermodynamics is applied to actual physical processes which are not quasi-static and the condition for the results to be valid is that the fractional energy loss per cycle shall be small. Provided this condition is satisfied, the fractional energy loss per cycle is given by 2μ, where μ is the amplitude absorption coefficient per wavelength. μ is given by the product of the amplitude absorption coefficient per unit length of path α, and the wavelength λ in the liquid. For example, in benzene $2\mu = 1{\cdot}6\%$ at 10 Mc/s.; as in all liquids of this type, μ is proportional to the frequency. The same difficulty occurs in considering gases, but the agreement between observed and calculated absorption is quite good over the whole dispersive range of frequencies.

The velocity of sound, Γ, is expressed by the Euler–Laplace relation

$$\Gamma^2 = (\delta p/\delta \rho)_{\text{adiab.}} \qquad \ldots\ldots(1)$$

where p is the pressure and ρ the density of the fluid. For a plane harmonic wave Γ is complex, and if α is the absorption coefficient per unit length of a wave propagated in the x-direction, then the wave motion is represented by

$$\exp\{i2\pi\nu(t - x/\Gamma)\} = \exp\{i2\pi\nu(t - x/c)\}\exp\{-\alpha x\}$$

so that

$$\alpha = -\pi c\nu \mathscr{I}\left[\frac{1}{\Gamma^2}\right] \qquad \ldots\ldots(2)$$

where ν is the frequency, c the measured velocity of sound which is equal to the real part of Γ and $\mathscr{I}(z)$ denotes the imaginary part of z. Because α is proportional to the square of the frequency, it is usual to consider α/ν^2 which is independent of frequency.

For an adiabatic change, the first law of thermodynamics is written in terms of the internal energy E and the enthalpy H

$$\delta E + p\delta V = 0; \qquad \delta H - V\delta p = 0 \qquad \ldots\ldots(3)$$

where

$$E = E' + \Sigma_j W_j a_j; \qquad H = H' + \Sigma_j W_j a_j, \qquad \ldots\ldots(4)$$

a_j is the fraction of molecules in the jth excited level of energy W_j, and primes refer to quantities excluding the contributions of the excited levels. All extensive quantities (E, H, W_j, V) are referred to one gram molecule as unit.

It is convenient to take the change in temperature produced at any point in the liquid by the sound wave as independent variable, and thus equations (1) and (3) give

$$\Gamma^2 = \frac{p}{\rho}\frac{(\partial H/\partial T)_S}{(\partial E/\partial T)_S}.$$

Using standard thermodynamical relations this gives

$$\Gamma^2 = \frac{p}{\rho}\frac{C_{\text{p}}/lT}{C_{\text{v}}p\kappa/lT}$$

where l is the coefficient of thermal expansion, κ is the isothermal compressibility, and C_{p} and C_{v} are the principal specific heats. The division of the thermodynamical functions into the contributions of external and internal degrees of freedom must be made at this stage, because it is assumed that the entropy of the whole assembly, $S = S' + \Sigma_j a_j S_j$, is conserved.* Thus we have

$$\Gamma^2 = \frac{1}{\rho\kappa}\frac{(C'_{\text{p}} + \Sigma_j W_j(\delta a_j/\delta T))}{(C'_{\text{v}} + \Sigma_j W_j(\delta a_j/\delta T))}. \qquad \ldots\ldots(5)$$

---

* I am indebted to Professor Herzfeld for pointing this out.

The vibrational specific heat, $\Sigma_j W_j(\delta a_j/\delta T)$, is the only quantity contributing to Γ which depends on time, so that with the present formulation it is the only complex quantity. Taking the vibrational specific heat to be much smaller than C_{p}'' and C_{v}', although this is not always the case, equations (2) and (5) give

$$\frac{\alpha}{\nu^2} = -\frac{\pi}{\nu}\frac{c}{c'^2}\frac{\gamma'-1}{C_{\mathrm{p}}'}\mathscr{I}[\Sigma_j W_j(\delta a_j/\delta T)] \qquad \ldots\ldots(6)$$

where γ is the ratio of the principal specific heats.

§3. THE RELAXING SPECIFIC HEAT

Because of the relatively high frequency of the sound wave the specific heat, $\Sigma_j W_j(\delta a_j/\delta T)$, differs slightly from its equilibrium value. Its value can be calculated most conveniently by setting up an equation of detailed balance and considering it under conditions of slightly perturbed equilibrium.

First, we shall consider a single excited level, j, in equilibrium with the ground state which is denoted by the suffix 0. Thus a_j, a_0 $(=1-a_j)$ are the fractions of molecules that are excited and unexcited respectively, and the equation of detailed balance may be written

$$\partial a_j/\partial t = a_0 k_{0j} - a_j k_{j0}, \qquad \ldots\ldots(7)$$

where the k_{ij} are rate constants. In equilibrium, $\partial a_j/\partial t = 0$, and therefore

$$a_j/a_0 = k_{0j}/k_{j0} = \exp(-W_j/RT). \qquad \ldots\ldots(8)$$

The perturbation is produced by plane harmonic sound waves of frequency $\nu = \omega/2\pi$. Thus writing $i\omega$ for $\partial/\partial t$ we get, from equations (7) and (8)

$$\delta(\partial a_j/\partial t) = i\omega\delta a_j = \delta(a_0 k_{0j} - a_j k_{j0}) = k_{j0}\delta(a_0 k_{0j}/k_{j0} - a_j)$$

provided the perturbation is small. Taking the temperature as independent variable, we obtain (Rutgers 1933)

$$\frac{\delta a_j}{\delta T} = \frac{W_j}{RT^2}a_j\left[1 + i\frac{\omega}{k_{j0}+k_{0j}}\right]^{-1}.$$

If we disregard the excitation of harmonics of the vibration it is consistent to neglect $\exp(-W_j/RT)$ compared with unity. This gives

$$\frac{\delta a_j}{\delta T} = \frac{W_j}{RT^2}[1 + i\omega/k_{j0}]^{-1}\exp(-W_j/RT) \qquad \ldots\ldots.(9)$$

and if the equilibrium value of the vibrational specific heat is denoted by C_j,

$$\mathscr{I}[W_j\delta a_j/\delta T] = -(\nu/\nu_j)C_j[1 + (\nu/\nu_j)^2]^{-1} \qquad \ldots\ldots(10)$$

where $\nu_j = k_{j0}/2\pi$ is the dispersion frequency of the jth level.

In the numerical applications which are given later, the Einstein specific heat $R(W_j/RT)^2\exp(W_j/RT)[\exp(W_j/RT)-1]^{-2}$ is used for C_j. It can be seen that, when $\exp(-W_j/RT)$ is neglected compared with unity, the Einstein specific heat reduces to the simple form of C_j given in equations (9) and (10). In the case of polyatomic substances there are always several vibrational levels, and equations corresponding to (7) and (8) can be written down for the case of l excited levels.

They are

$$a_j = a_0 \exp(-W_j/RT); \qquad \partial a_j/\partial t = \sum_{i=0,\, i\neq j}^{l} [a_i k_{ij} - a_i k_{ji}] \qquad \ldots\ldots(11)$$

where $j = 1, 2, \ldots l$ and a fraction a_j of the molecules is excited with energy W_j; k_{ij} is the rate constant corresponding to an $i \rightarrow j$ transition.

Proceeding as before, we find $(l+1)$ linear simultaneous equations in the $(l+1)$ variables $\delta a_i/\delta T$;

$$\left.\begin{aligned} [(\sum_{i\neq j} k_{ji}) + i\omega]\delta a_j/\delta T - \sum_{i\neq j} k_{ij}\delta a_i/\delta T = \sum_{i\neq j} a_i k_{ij}(W_j - W_i)/RT^2 \\ \sum_{i=0}^{l} \delta a_i/\delta T = 0. \end{aligned}\right\} \qquad \ldots\ldots(12)$$

In principle there is no difficulty in solving these equations, but there are $l(l+1)$ quantities k_{ij} with $\frac{1}{2}l(l+1)$ relations of type (8) between them, and as the k_{ij} are unknown quantities (see § 5), it is not practicable to solve equations (12).

Because there are l excited levels, the vibrational specific heat can be expressed (Kronig 1938) as a sum of l terms of the type

$$\sum_{j=1}^{l} \frac{C_j}{1 + i\nu/\nu_j} = \frac{\Sigma C_j}{1 + i\nu/\nu_{\mathrm{m}}} \qquad \ldots\ldots(13)$$

where the most important contribution to ν_j is $k_{j0}/2\pi$. Results have generally been expressed in terms of a mean dispersion frequency ν_{m} defined by equation (13); from various considerations it appears very improbable that in liquids like carbon disulphide and benzene all vibrational levels relax at the same frequency, so that ν_{m} has no detailed physical meaning, although it does give the order of magnitude of the dispersive frequency range in a liquid.

From equations (6) and (13), the absorption coefficient is given by

$$\frac{\alpha}{\nu^2} = \pi \frac{c}{c'^2} \frac{\gamma' - 1}{C'_{\mathrm{p}}} \frac{\Sigma C_j}{\nu_{\mathrm{m}}} \frac{1}{1 + (\nu/\nu_{\mathrm{m}})^2}. \qquad \ldots\ldots(14)$$

Equation (9) shows that when ν is very much larger than ν_j, the effective vibrational specific heat $\Sigma_j W_j \delta a_j/\delta T$ becomes negligibly small, and so primed quantities, which do not include the contribution of the vibrational levels, correspond to the case $\nu \gg \nu_{\mathrm{m}}$.

§ 4. THE MEAN DISPERSION FREQUENCY

Equation (14) can be used to give values of the mean dispersion frequency for different liquids by substituting experimental values of α/ν^2. The results for a number of liquids are recorded in Table 1.

What has actually been calculated is μ_{m}, the absorption coefficient per wavelength at $\nu = \nu_{\mathrm{m}}$, which is given by

$$\mu_{\mathrm{m}} = \frac{\pi}{2} \frac{\gamma}{\gamma'} \frac{\gamma' - 1}{C'_{\mathrm{p}}} \Sigma C_j, \qquad \ldots\ldots(15)$$

and the mean dispersion frequency ν_{m} is calculated from the relation

$$\nu_{\mathrm{m}} = (2\mu_{\mathrm{m}}/c)[1/(\alpha/\nu^2)_{\nu \ll \nu_m}] \qquad \ldots\ldots(16)$$

which was given by Kneser (1938) and has been used by Pinkerton (1949) to obtain approximate estimates for $\nu_{\rm m}$. However, both from experimental results (Rapuano 1947) and from a consideration of temperature coefficients of absorption (§6), as well as of transition probabilities which determine the dispersion frequencies ν_j of the individual vibrational levels (§5) it appears that all levels do not in fact relax together, so that while equation (15) defines some quantity $\mu_{\rm m}^*$ which, when substituted in (16) gives the correct $\nu_{\rm m}$, yet $\mu_{\rm m}^*$ is not the absorption coefficient per wavelength at $\nu=\nu_{\rm m}$. It follows that $2\mu_{\rm m}^*$ does not give the fractional energy loss per cycle at dispersion and thus the method used by Pinkerton (1949) in estimating $\nu_{\rm m}$, while interesting and good to an order of magnitude, cannot be regarded as supported in detail by the present considerations.

Table 1. Mean Dispersion Frequencies of some Liquids, calculated from Equation (16). All values refer to 300° K.

Substance	a/ν^2 (1)	c (2)	c' (3)	C (4)	$2\mu_{\rm m}^*$ (5)	$\nu_{\rm m}$ (6)
Carbon disulphide	10,800 (*a*)	1·14 (*f*)	1·25	4·00	0·644	52·5
Benzene	830 (*b*)	1·31 (*b*)	1·53	11·7	1·300	1,200
Carbon tetrachloride	513 (*b*)	0·910 (*b*)	1·09	12·3	1·593	3,420
Chloroform	380 (*c*)	0·987 (*c*)	1·10	7·84	0·835	2,230
Toluene	84 (*c*)	1·31 (*c*)	1·44	(13·0)	0·823	7,500
Acetone	60 (*c*)	1·17 (*c*)	1·27	7·50 (*e*)	0·614	8,720
Ethyl bromide	56 (*b*)	0·932 (*b*)	1·07	(8·0)	1·137	21,800

(1) Experimental values of absorption a/ν^2 (sec^2 cm$^{-1}\times10^{-17}$)†.
(2) Experimental values of velocity c (cm. sec$^{-1}\times10^5$) ($\nu\ll\nu_{\rm m}$).
(3) Calculated value of c', the velocity at frequencies $\nu\gg\nu_{\rm m}$ (cm. sec$^{-1}\times10^5$).
(4) Vibrational specific heat C_j (cal/mole deg.) (*d*).
(5) Values of $2\mu_{\rm m}^*$ from equation (15).
(6) Mean dispersion frequency $\nu_{\rm m}$ (Mc/s.).

(*a*) Kneser (1938).
(*b*) Pellam and Galt (1946).
(*c*) Willard (1941).
(*d*) Herzberg (1945).
(*e*) Schumann and Aston (1938).
(*f*) Biquard (1935).

† The value of a/ν^2 due to viscosity and heat conduction has been subtracted.

It may be convenient to give here the formula for the dependence of the velocity on frequency, which is of course the real "dispersion" formula. From equations (4) and (8) we obtain

$$c_\nu{}^2=c'^2\left[1-\frac{\Sigma C_j}{1+(\nu/\nu_{\rm m})^2}\frac{\gamma'-1}{C'_{\rm p}}\right] \qquad \ldots\ldots(17)$$

since $\Sigma_j W_j\delta a_j/\delta T\ll C'_{\rm p}, C'_{\rm v}$. This equation shows that $\lim_{\nu\to\infty} c_\nu=c'$, as has already been inferred from physical considerations.

§5. THEORETICAL ESTIMATES OF THE DISPERSION FREQUENCY

From equations (9) and (10) it can be seen that to calculate ν_j the essential step is the calculation of k_{j0}, the rate at which a molecule in the *j*th excited vibrational level falls back into the ground state. There is no reason to believe that there exists a potential barrier large compared with $\boldsymbol{k}T$ to prevent de-excitation

(Eucken and Becker 1934), so that the rate constant k_{j0} is given by the product of the collision frequency ν_{coll} and the transition probability p_{j0}. For a gas, the collision frequency can be calculated from the mean free path and mean velocity of the molecules; at room temperature and atmospheric pressure $\nu_{\mathrm{coll}} \sim 5 \cdot 10^9\ \mathrm{sec}^{-1}$. For liquids, $\nu_{\mathrm{coll}} \sim \boldsymbol{k}T/\boldsymbol{h}$ (Glasstone, Laidler and Eyring 1941) which is of the order $10^{12}\ \mathrm{sec}^{-1}$ at 300° K. The observed dispersion frequencies for gases lie in the range 10^3–10^6 c/s., and predicted values for liquids are of the order 10^9–10^{10} c/s. Thus the transition probabilities lie in the ranges 10^{-6} to 10^{-3} for gases and 10^{-3} to 10^{-2} for liquids.

The low value of this transition probability in the case of a gas has been explained by Zener (1931), who showed that it is a consequence of the quantal treatment of collisions between an atom and a vibrating molecule that inelastic collisions are infrequent. Later, Landau and Teller (1936) derived an approximate classical formula for the dispersion frequency, but their result is not applicable at room temperature where the spacing of the vibrational levels is relatively large compared with $\boldsymbol{k}T$.

In the case of liquids it is easy to modify Zener's treatment by adding a constant attractive potential U_0, representing the cohesion, to the Lennard-Jones repulsion between molecules, $E_0 \exp[-\alpha(r-r_0)]$ which of course depends very strongly on r, the distance apart of the molecules. Then, if ϵ_j is the energy of the jth level and K is the kinetic energy of the colliding particles before the impact, the transition probability is given by

$$p_{j0} = \frac{\pi^2}{16} \frac{\mu}{\mu_{\mathrm{m}}} \frac{E_0}{\epsilon_j} \left(\frac{K+U_0}{K+U_0+\epsilon_j} \right)^{\sqrt{(uE_0)}\,.\,2/\alpha} \qquad \ldots\ldots(18)$$

where all quantities are measured in atomic units, and μ and μ_{m} are reduced masses of the system as a whole and the vibrating molecule respectively. An outline of the derivation of (18) is given in the appendix where order of magnitude values for the various quantities are indicated. They give values of p_{j0} which are of the correct order (10^{-3} to 10^{-2}) and in view of the idealizations and approximations of the analysis no detailed deductions can usefully be made; in particular, the difference in the behaviour of different substances cannot be explained because no account is taken of the structure of the colliding particles or of dipole moments which produce an increase in the transition probabilities (Metter 1937). From equation (18) it can be seen that p_{j0} decreases with increasing energy of excitation ϵ_j and, as both K and U_0 are of the order $3\boldsymbol{k}T/2$, the transition probability increases with increasing temperature.

Eucken and Becker (1934) found that the transition probability in gaseous mixtures increases as the third or fourth power of the temperature. In an attempt to explain the inefficiency of collisions they showed that if the efficiency of a collision is inversely proportional to the $2n$th power of the closest distance of approach of the molecules, then this transition probability is proportional to T^n. Exactly the same temperature variation results if one supposes that the efficiency of a collision is proportional to the nth power of the mutual kinetic energy of the particles before impact. In the case of liquids this picture again has a qualitative significance, but because of the interaction represented by U_0, the value of n will be rather smaller, of the order 1 to 2.

§6. THE TEMPERATURE COEFFICIENT OF ABSORPTION

We write equation (14) in the form

$$\frac{\alpha}{\nu^2} = \text{const.}\, \frac{(\gamma' - 1)}{c} \frac{\Sigma C_j}{\nu_m} \qquad \ldots\ldots(14\,a)$$

where the constant, $\pi\gamma/\gamma' C'_p$, is approximately independent of temperature, while by a standard thermodynamic result $(\gamma' - 1)$ is proportional to T. Now it is convenient to write $\partial \log C_j/\partial T = D_j/T$ where $D_j \simeq W_j/RT - 2$ for $W_j \gg RT$ and $\partial \log \Sigma C_j/\partial T = \bar{D}/T$. It has been seen that the transition probability increases with temperature, approximately as T^n, where n is of order 1 to 2. The collision frequency, $\boldsymbol{k}T/\boldsymbol{h}$, is proportional to T, and logarithmic differentiation of equation (14 *a*) gives

$$\frac{1}{\alpha}\frac{\partial \alpha}{\partial T} = \frac{-1}{c}\frac{\partial c}{\partial T} + \frac{1}{T}[\bar{D} - n]. \qquad \ldots\ldots(19)$$

By consideration of Table 2 we see that, for this equation to be satisfied, n would have to be much less than one or negative in many cases. These values cannot be reconciled with equation (18), or with simple physical considerations like those of Eucken and Becker.

Table 2. Temperature Coefficients of Absorption

Substance	10^{+3} deg^{-1}* (1)	10^3 deg^{-1} (2)	$(D-n)_{\text{eff}}$ (3)	$\bar{D} = T\partial \log \Sigma C_j/\partial T$ (4)
Carbon disulphide	(10)	−(3·5)	+1·95	0·874
Benzene	11 (*a*)	− 3·6 (*a*)	+2·22	1·820
Carbon tetrachloride	(0)	−(3·5)	−1·05	0·623
Chloroform	(10)	− 3·4 (*b*)	+1·98	0·660
Acetone	(10)	− 3·8 (*b*)	+1·86	1·840
Ethyl bromide	10 (*a*)	− 3·6 (*a*)	+1·92	(1·0)

(1) Measured values of temperature coefficients of absorption (10^3 deg^{-1}).
(2) Measured values of temperature coefficients of velocity (10^3 deg^{-1}).
(3) $(D-n)_{\text{eff}}$ calculated from equation (19).
(4) $\bar{D} = T\partial \log \Sigma C_j/\partial T$ (see § 6).

(*a*) Pellam and Galt (1946). (*b*) Willard (1941).

* Experimental values for temperature coefficients of absorption are rather incomplete, but for unassociated liquids the values are generally near (+)10^{-2} deg^{-1}; carbon tetrachloride is an exception, as here the absorption seems to vary very little with temperature (Bazulin 1937).

The difficulty can be overcome if we suppose that the individual levels relax one by one, a high excited level having a low probability of de-excitation and thus a low dispersion frequency. Because a high excited level has a low specific heat but a large temperature coefficient of specific heat, the change in weight of the several levels arising from the replacement of

$$\partial[\log(\Sigma C_j/\nu_m)]/\partial T \quad \text{by} \quad \partial[\log(\Sigma\, C_j/\nu_j)]/\partial T$$

would result in a larger value of $(D-n)_{\text{eff}}$.

Unfortunately there are no data available on the values of ν_j, but there are several independent results which show that in certain cases different vibrational levels relax at different frequencies. Acetaldehyde vapour (Alexander and Lambert 1942) shows three distinct dispersion regions, which the authors ascribe to the relative complexity of the molecule.

The behaviour of liquid carbon disulphide is of special interest, because it is the most highly absorbing simple liquid which has been investigated. A study of the absorption coefficients measured at different frequencies shows that multiple dispersions must be assumed to explain the results which are given in Table 3A.

In Table 3B these results are interpreted in the light of the previous discussion and the dispersion frequencies of the three vibrational levels are calculated.

Table 3. Multiple Dispersion in Carbon Disulphide

A: Experimental values of the absorption

α/ν^2 (cm^{-1} sec$^2 \times 10^{-17}$)	$10{,}750 \pm 1{,}000$	7,400	1,400
Frequency (Mc/s.)	<1	6·5	75,105
Observer	Claeys, Errera, Sack quoted from Kneser (1938)	Willard (1941)	Rapuano (1947)

B: Interpretation of these results

Vibrational level frequency (cm^{-1})	Vibrational specific heat, C_j (cal/mole deg.)	Velocity c ($\nu \ll \nu_j$) (cm. sec^{-1} $\times 10^5$)	Velocity c' ($\nu \gg \nu_j$) (cm. sec^{-1} $\times 10^5$)	$2\mu_j$ [cf. eq. (15)]	$\Delta(\alpha/\nu^2)$ (cm^{-1} sec^2 $\times 10^{-17}$)	ν_j (Mc/s)
1523	0·0724	1·14	1·14	0·00705	3,350	1·85
656,5	0·930	1·14	1·157	0·106	6,000	15·5
397 (doublet)	3·00	1·157	1·245	0·494	1,400	305

It is now possible to evaluate

$$D_{\text{eff}} = \frac{T}{\Sigma C_j{}' \nu_j} \frac{\partial C_j}{\partial T} \Sigma \frac{1}{\nu_j}$$

for carbon disulphide on the basis of Table 3B. The value obtained is 2·76, so that if n is taken equal to one, $(1/\alpha)(\partial\alpha/\partial T) \simeq 9 \cdot 10^{-3}$ deg^{-1}.

§7. BINARY MIXTURES

It is well known that in the case of gases small traces of impurities may have an extremely large effect on the absorption (Eucken and Becker 1934). A similar effect has been found in a number of liquids like carbon disulphide and benzene where the absorption falls very rapidly when a small quantity of a less absorbing liquid is added to one of high absorption. Pinkerton (1949) has shown that this effect can be explained on a very simple relaxation picture. It is shown here how the same basic ideas, when interpreted in terms of transition probabilities, yield results which are in good agreement with experiment.

Let A be the strongly absorbing liquid and B the other one. Then A has a much smaller dispersion frequency than B, so that an A molecule, once excited, has a much smaller chance of de-excitation than an excited B molecule. For simplicity in the analysis it will be assumed that only binary collisions need be considered and that collisions between excited molecules may be neglected. Then if A and A* represent an unexcited and an excited A molecule respectively, and similarly for B, B*, then an (A*A) collision is much less efficient than a (B*B) collision because $\nu_{\text{m}}^{\text{A}}$ is much smaller than $\nu_{\text{m}}^{\text{B}}$. In a mixture of molecules of both species, A and B, there will, in addition to (A*A) and (B*B) collisions also be (A*B) and (B*A) impacts which have a rather high de-excitation efficiency because it is in general impossible for a quantum of vibrational energy to be transferred from one type of molecule to the other without some loss of energy. Now, following Pinkerton, we make the crucial assumption that (A*B) and (B*A) collisions are as efficient in producing excitation and de-excitation as (B*B) collisions. Thus, as the concentration of B molecules increases, the net efficiency of all collisions tends rapidly to the value corresponding to the liquid B, so that the absorption falls sharply.

In the analysis it is convenient to suppose that each molecular species has only a single excited level of energy W_{A} and W_{B} for A and B respectively. The generalization for a number of levels proceeds as in § 3 for the case of a single liquid, and the same approximation is made.

Consider 1 gm. mol. of the mixture; a fraction a is made up of A molecules, there being mole fractions a_1, $a_0(=a-a_1)$ of excited and unexcited molecules, and similarly mole fractions b_1, b_0 for the liquid B, where $a+b_1+b_0=1$. Introducing k, g, l and h respectively as (AA), (AB), (BA) and (BB) transition probabilities, we can write two equations of detailed balance:

$$\left.\begin{aligned}\frac{\partial a_1}{\partial t}&=(k_{01}a_0+g_{01}b_0)a_0-(k_{10}a_0+g_{10}b_0)a_1=\phi_{01}a_0-\phi_{10}a_1\\ \frac{\partial b_1}{\partial t}&=(l_{01}a_0+h_{01}b_0)b_0-(l_{10}a_0+h_{10}b_0)b_1=\psi_{01}b_0-\psi_{10}b_1\end{aligned}\right\}. \quad \ldots\ldots(20)$$

Proceeding as in § 3, one arrives at the result

$$\left.\begin{aligned}\partial a_1/\partial T&=(W_{\text{A}}/RT^2)a[1+i\omega/\phi_{10}]^{-1}\exp(-W_{\text{A}}/RT)\\ \partial b_1/\partial T&=(W_{\text{B}}/RT^2)(1-a)[1+i\omega/\psi_{10}]^{-1}\exp(-W_{\text{B}}/RT]\end{aligned}\right\}, \quad \ldots\ldots\ldots(21)$$

and if C_{A}, C_{B} denote the vibrational specific heats of A and B, equation (13) becomes

$$\left(\frac{\alpha}{\nu^2}\right)_a=2\pi\left[\frac{\pi c}{c'^2}\left(\gamma'-1\right)\frac{1}{C'_{\text{p}}}\right]_a\left[\frac{aC_{\text{A}}}{\phi_{10}}+\frac{(1-a)C_{\text{B}}}{\psi_{10}}\right]. \quad \ldots\ldots(22)$$

Now two approximations are introduced:

(i) The crucial assumption that, to a first approximation, (B*B), (B*A), (A*B) collisions are all equally efficient in producing an inelastic transition, z times ($z\sim10$) more so than (A*A) collisions. In mathematical form this is written $zk_{ij}=g_{ij}=l_{ij}=h_{ij}$ $(i, j=0, 1)$.

(ii) The quantity $2\pi^2\frac{c}{c'^2}\left(\gamma'-1\right)\frac{1}{C'_{\text{p}}}$ changes linearly with concentration a. This is not a critical assumption because the total variation in this quantity is not large. It will be written $M_{\text{B}}(1-fa)$.

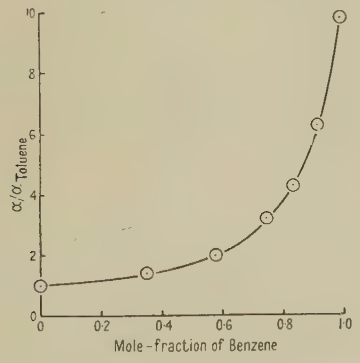
Then equation (22) becomes

$$(\alpha/\nu^2)_a=(M_{\text{B}}/g_{10})(1-fa)[(1-a)C_{\text{B}}+azC_{\text{A}}/\{z-a(z-1)\}]$$

which can conveniently be compared with experiment in the form

$$\frac{\alpha_A}{\alpha_B}=(1-fa)\left[(1-a)+\frac{az}{z-a(z-1)}\frac{C_A}{C_B}\right]. \qquad \ldots\ldots(23)$$

Results for a benzene–toluene mixture are given in the Figure. If A specifies benzene and B toluene then, using the values given in Table 1, f and z are given by $f=1-\frac{\alpha_A}{\alpha_B}\frac{C_B}{C_A}\frac{1}{z}=-0{\cdot}743$ and $z=\nu_m^B/\nu_m^A=6{\cdot}28$ since $C_A/C_B=0{\cdot}904$ and $\alpha_A/\alpha_B=9{\cdot}80$. Pinkerton's (1949) result is recovered by putting $f=0$ and $C_A=C_B$ so that $z=\alpha_A/\alpha_B$.



Ratio of the absorption coefficient of a mixture of benzene and toluene to the absorption coefficient of toluene as a function of the mole fraction of benzene.

Full line : theoretical curve (equation (23)).

Circles : experimental points (Grobe 1938).

§ 8. DISCUSSION

Since the present approach to the problem of vibrational relaxation is based on rather general considerations regarding the perturbation of an equilibrium, the same general method can be applied to a number of different aspects of the problem of incomplete excitation of some internal degree of freedom of the molecules. In particular, the application to the perturbation of a chemical equilibrium by the sound wave is of interest. Such an effect may be the cause of the dispersion observed in acetic acid by Spakovskij (1938) and others. Pinkerton (1948), using his own and Bazulin's (1936) results for the absorption of sound in acetic acid near 2 Mc/s., has estimated by a graphical method that the fall in α/ν^2 in this frequency range is $12{,}000\times10^{-17}$ cm^{-1} sec^2 and that the dispersion frequency is 2 Mc/s. at 17° c. From these data a value of the relaxing specific heat can be calculated from equation (14): its value is 1·4 cal/mole degree. This is very large and might correspond to a hindered rotation or similar process.

§ 9. CONCLUSIONS

In the case of simple, unassociated polyatomic liquids like benzene, incomplete excitation of the vibrational degrees of freedom by the sound wave is shown to lead to a dispersion, with mean dispersion frequencies in the range 10^9 to 10^{10} c/s. at room temperature. It does not seem probable that all vibrational levels of a liquid relax together: it is possible that some high excited levels have dispersion frequencies below 10^7 c/s. which have not so far been detected. Carbon disulphide may well be a case in point, for consideration of the available experimental data indicates that its three vibrational levels may have dispersion frequencies of 1·85, 15·5 and 305 Mc/s.

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APPENDIX

Calculation of Transition Probabilities

A brief outline of Zener's (1931) treatment is presented here, with a modification to account for the cohesive forces in a liquid. To facilitate reference to the original paper a similar notation is employed and atomic units are used.

Zener considers the one dimensional collision of an atom A of mass M_A with a vibrating molecule B–C, the two atoms of this having masses M_B and M_C. By a suitable choice of coordinates the motion of the centre of mass becomes separable and is eliminated, and the wave equation of the system is written

$$\left[\frac{1}{\mu_m}\frac{d^2}{dx^2}+\frac{1}{\mu}\frac{d^2}{dr^2}-V(x)-U(x,r)+E\right]\Psi=0. \qquad \ldots\ldots(24)$$

Here r is the coordinate describing the position of A relative to the centre of mass BC, x is the distance BC between the vibrating atoms, $\mu_m=M_B M_C/(M_B+M_C)$ and $\mu=M_A(M_B+M_C)/(M_A+M_B+M_C)$ are the reduced masses of the vibrator BC and the whole system respectively; E is the total energy of the system, $V(x)$ the potential energy of the vibrator, and $U(x, r)$ the mutual potential energy of atom A and molecule BC. The modification which has been made to Zener's treatment is that a constant attractive term $-U_0$ is added to the repulsive term $V(x, r)$ which depends strongly on distance. U_0 must be present, and rather larger than $3\boldsymbol{k}T/2$, for the liquid to maintain its volume.

$$U(x,r)=-U_0+V(x,r). \qquad \ldots\ldots(25)$$

The vibrational motion of (BC) in its ith state is described by the wave equation

$$[(1/\mu_m)(d^2/dx^2)-V(x)+E_i]\phi_i(x)=0 \qquad \ldots\ldots(26)$$

where $\phi_i(x)$ is the normalized wave function corresponding to the energy E_i.

Now, define the momentum, p_i, by

$$p_i=[\mu(E+U_0-E_i)]^{\frac{1}{2}}. \qquad \ldots\ldots(27)$$

We require a solution of (27) having the asymptotic form

$$\Psi(r\rightarrow\infty)=\frac{e^{ip_i r}+e^{-ip_i r}}{p_i^{\frac{1}{2}}}+\sum_f \gamma_{if}\frac{e^{-ip_f r}}{p_f^{\frac{1}{2}}}\phi_f(x). \qquad \ldots\ldots(28)$$

This solution of course consists of an incident wave which is scattered, in part inelastically: the probability of a change $i\rightarrow f$ in vibrational quantum number is $|\gamma_{if}|^2$.

To obtain γ_{if}, we must find a solution for (24) of the form (28). The wave function is expanded as $\Psi = \sum_k Q_k(r)\phi_k(x)$, the $Q_k(r)$ being undetermined functions. This is substituted in equation (27) and after multiplying by $\phi_j(x)$ and integrating over x, the orthonormality of the ϕ_j leads to

$$\left[\frac{d^2}{dr^2} - \mu V_{kk} + p_k^2\right] Q_k(r) = \mu \sum_{j \neq k} Q_j(r) V_{kj}(x) \qquad \ldots\ldots(29)$$

where $V_{ij}(r) = \int \phi_i(x) V(x, r) \phi_j(x)\, dx$.

Born's collision method is now used to obtain approximate solutions of (29); first the right hand side of (29) is put equal to zero and the zero-order solution, $Q_k^{(0)}(r)$, corresponding to elastic scattering is found. Then $Q_k^{(0)}(r)$ is substituted on the right hand side and the equation solved again, to give the first order approximation, $Q_k^{(1)}(r)$ which is the one used.

The remainder of Zener's treatment is purely mathematical. In order to obtain a relatively simple set of solutions of equation (29), he replaces the potential $V_{kk} = E_0 \exp\{-\alpha(r - r_0)\}$ by an inverse square law which fits the exponential function in the critical region where $r \sim r_0$. This enables the solution of (29) to be found in terms of Bessel functions and finally gives the transition probability for de-excitation of the first excited state of the jth level, of energy ϵ_j,

$$p_{j0} = |\gamma_{10}^{(j)}|^2 = \frac{\pi^2}{16} \frac{\mu}{\mu_{\mathrm{m}}} \frac{E_0}{\epsilon_j} \cdot \left(\frac{p_i}{p_f}\right)^{\sqrt{(\mu E_0)}\,.\,4/\alpha}. \qquad \ldots\ldots(30)$$

If one writes $E - E_i = K$, the relative kinetic energy of the atom A relative to the molecule BC before impact, equation (27) gives

$$p_{j0} = \frac{\pi^2}{16} \frac{\mu}{\mu_{\mathrm{m}}} \frac{E_0}{\epsilon_j} \left(\frac{K + U_0}{K + U_0 + \epsilon_j}\right)^{\sqrt{(\mu E)}\,.\,2/\alpha}. \qquad \ldots\ldots(18)$$

Substitution of numerical values shows that this expression gives results which are of the correct order of magnitude. Taking A, B and C to be each of molecular weight 50, $E_0 = \boldsymbol{k}T$, $K = U_0 = 3\boldsymbol{k}T/2$, $\epsilon_j \doteq 3\boldsymbol{k}T$ at 300° K. ($\simeq 625$ cm^{-1}) then for α equal to 2 and 3 in atomic units the corresponding values* of p_{j0} are $6{\cdot}04 \times 10^{-3}$ and $3{\cdot}12 \times 10^{-2}$.

Note added in proof (8*th January* 1949). The treatment of transition probabilities which is outlined in the appendix cannot be regarded as completely satisfactory in its application to liquids, as it is but a modification of the corresponding analysis for a gas. It would be better to use a quasi-crystalline model of a liquid, and work on this is proceeding.

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[*] Jackson and Mott (1932) have pointed out that there is a factor 4 missing in Zener's equation corresponding to equation (30) of this paper. This factor has been allowed for here.

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Second Sound and the Behaviour of Helium II

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ABSTRACT. In this paper some theoretical consequences of the existence of second sound in helium II are discussed. A method is suggested for setting up a quantitative phenomenological description of the thermodynamical behaviour of helium II. It is known that expressions for the velocities of first and second sound may be obtained by using quite general models. The thermodynamical behaviour may be described in terms of the velocities of these two types of sound, so that it becomes possible, in principle, to obtain explicit values of the unknowns by combining the two sets of equations. On the basis of these ideas a discussion is given of the coefficient of thermal expansion of helium, the ordinary thermal conductivity, and the attenuation of second sound.

The paper contains a discussion of the modifications necessary to the Debye theory of specific heats when the sound velocities are temperature-dependent.

§ 1. PREVIOUS THEORIES OF THE THERMODYNAMICAL BEHAVIOUR OF HELIUM II

It is well known that liquid helium at very low temperatures possesses anomalous properties. At 2·19° K., the λ-point, a phase change of the second order takes place, and below this temperature the liquid, known as helium II, possesses properties rather similar in nature to those of superconductors. Details of these properties may be found in Keesom's book on helium (Keesom 1942). A particular property with which we shall be concerned in this paper is that below the λ-point the values of the entropy and the specific heat of the liquid are very much larger than the values to be expected from Debye's theory (Debye 1912), calculated from the known values for the velocity of ordinary sound in the liquid. Theories have been suggested by several authors to account for these properties; we may mention in particular those of London (1938, 1939), Tisza (1938, 1940, 1947), Landau (1941), and Green (1948).

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The ideas of London and Tisza are based on the concept of a Bose-Einstein condensation, a phenomenon predicted theoretically for an ideal gas (London 1938, 1939, Fowler and Jones 1938, Dingle 1949). According to this theory, below a certain very low temperature a fraction of the available atoms become condensed into the lowest available state. These authors believe that many of the peculiar properties of this ideal Bose-Einstein gas may be taken over into the theory of liquid helium. However, it must be stressed that the theory is only a qualitative one, since the values of the entropy as a function of temperature given by ideal gas theory are too inaccurate to be of value, the entropy being given as proportional to $T^{1\cdot 5}$ as opposed to the experimental relation $S \propto T^{5\cdot 5}$. In order to obtain reasonable agreement with experiment, the model must be altered in an empirical manner.

Landau's general theory of helium (Landau 1941) is based on his quantum hydrodynamics, which is an attempt in quantum theory to avoid the difficulties of a complete microscopic theory of fluids in a similar way to that in which they are avoided by classical hydrodynamics. Landau concludes that only discrete values of the curl of the velocity are permitted, and that there will be a gap in the energy spectrum associated with these "roton" excitations. The entropy will be contributed by ordinary Debye waves (phonons) and by these rotons. The phonon contributions are calculated in the usual manner. In order to derive the roton contributions, Landau assumes that only the first gap in the roton energy spectrum is of importance, and the excited levels are replaced by a continuum for which the energy ϵ is given by $\epsilon = \Delta + p^2/2\mu$, where Δ is the energy gap, p the momentum, and μ the effective mass of a roton. Thus in Landau's theory we have still two arbitrary parameters Δ and μ, which must be fixed by appeal to experiment.*

The very recent work of Green (1948) is based on the general kinetic theory of liquids developed by himself and Born (Born and Green 1946, 1947 a, b, Green 1947, 1948). On quantization it appears that pressure defined thermodynamically is no longer identical with pressure defined by kinetic theory. Green believes that many of the peculiar properties of liquid helium may be explained as due to this difference. Unfortunately, the detailed theory proves too complicated for direct application, and Green's results (e.g. the magnitude of this pressure difference) have in fact to be derived from experiment rather than from theory.

§ 2. QUALITATIVE DISCUSSION OF THE THEORY PROPOSED

The London-Tisza model, based on the concept of Bose-Einstein condensation, and the Landau theory, based on quantum hydrodynamics, agree both between themselves and with experiment in so far as the helium II is considered rather as a mixture of normal fluid and superfluid. On the London-Tisza model, the superfluid is supposed to consist of atoms which have piled up in the ground state, due to some kind of Bose-Einstein condensation, and the normal fluid to consist of the remaining atoms, i.e. those in the excited states. On the Landau theory, the superfluid is likewise made up of atoms in the ground state, whilst the normal fluid is described by excitations of Debye waves (phonons) and excitations of vortices (rotons). In both theories the entropy of the superfluid is of order zero, since only atoms in the ground state are involved. Tisza and Landau have shown independently that in a fluid of this nature we should expect two types of sound: ordinary "first" sound caused by the movement of the normal and superfluid together, and a new type, "second" sound, caused by relative movement of normal and superfluid. In second sound, owing to the relative movement of normal fluid, which carries entropy, and superfluid, which does not, we obtain a state of the liquid such that alternate layers contain an excess or a deficit of entropy. It follows that these layers are respectively at an effectively higher and lower temperature. The most important difference between the two types of sound is that the dominating feature in first sound is fluctuation in pressure, whilst in second sound it is fluctuation in temperature. Similar conclusions have also been reached by Green (1948).

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* In a recent variant of the theory there are three parameters (Landau 1947).

On two-fluid types of model, the velocity u_2 of second sound is given by $u_2^2 = TS^2\rho_s/C\rho_n$, where T is the temperature, S the entropy per gramme, C the specific heat per gramme and ρ_s/ρ_n the ratio of the densities of superfluid and normal fluid. In previous theories, more specialized models, or empirical formulae, have been used to calculate the values of S, C and ρ_s/ρ_n, and hence of u_2 as a function of temperature. In this paper we suggest a method by which these special models may be avoided. The argument is that a quantitative thermodynamical description of helium II may be given in terms of the velocities of the two kinds of sound by employing an extension of Debye's theory of specific heat: this gives us the values of S, C and ρ_s/ρ_n in terms of u_2, assuming that these two types of sound provide the dominant contributions to the thermal energy. In principle we have only to combine these equations with that giving u_2 in terms of the thermodynamical quantities to enable us to determine all the unknowns. In practice it will be much easier to show that the experimental values of u_2 are consistent with both sets of equations.

We shall encounter three main difficulties. Firstly, we know that there are $3N$ degrees of freedom per unit volume, where N is the number of atoms per unit volume. Thus there are $3N$ normal independent modes of vibration per unit volume : our problem is that of allocating these between first and second sound. A similar difficulty arises in the usual Debye theory, namely the question of the allocation of the available modes between longitudinal and transverse waves. Here some authors have made the arbitrary assumption that the frequency limits of the two types of waves may be taken to be the same; Brillouin (1936) and Lucas (1937) have shown that the assumption of equal wavelength limits is probably preferable. In our case this difficulty is not serious, as we shall find that second sound contributions are of overwhelming importance in the temperature region so far investigated.

Secondly, the usual Debye theory giving the thermodynamical behaviour in terms of the velocities of sound is only valid if these velocities are independent of temperature, the substance being at constant volume. This condition is roughly satisfied for first sound, but not for second sound, particularly near the λ-point. We shall discuss this problem in §§ 8 and 9 of this paper.

The third difficulty is that of determining how to take into account the absorption and dispersion of sound waves, as it is known that these effects become important as the λ-point is approached.

§ 3. THE DEBYE THEORY

Debye (1912) considers that in solids (and liquids) waves of sound will be present continually, the frequencies represented being those up to a certain limit dictated by the atomic structure of the material. This upper limit may be calculated from the fact that a real solid (or liquid) has only a finite number of degrees of freedom, so that we must cut off the upper end of the frequency spectrum to make the theory correspond. Physically, this corresponds to the idea that if the wavelength of the supposed Debye waves were shorter than the interatomic distance, the vibrations of shorter wavelength would not be independent of those of longer wavelength, since it is always possible to represent displacements of a finite number of particles equally well by an infinite number of vibrations of wavelength shorter than the interatomic distance.

For a single sound velocity c, independent of temperature, the Debye theory yields the following values for the thermodynamical quantities in which we are interested (see § 8):

$$\frac{E}{T}=9R\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3\,dx}{e^x-1}, \qquad \ldots\ldots(1)$$

$$S=3R\left[4\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3\,dx}{e^x-1}-\ln\left(1-e^{-\theta/T}\right)\right], \qquad \ldots\ldots(2)$$

$$C=9R\left[4\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3\,dx}{e^x-1}-\frac{\theta/T}{e^{\theta/T}-1}\right], \qquad \ldots\ldots(3)$$

where here C is the specific heat (at constant volume) per molecular volume. θ is the Debye characteristic temperature given by the relation

$$\boldsymbol{k}\theta=c(9N\boldsymbol{h}^3/4\pi)^{\frac{1}{3}}. \qquad \ldots\ldots(4)$$

At sufficiently low temperatures, $T\ll\theta$, we may use the simpler expressions

$$E/T=9R(T/\theta)^3\,\pi^4/15, \qquad \ldots\ldots(5)$$

$$S=12R(T/\theta)^3\,\pi^4/15, \qquad \ldots\ldots(6)$$

$$C=36R(T/\theta)^3\,\pi^4/15. \qquad \ldots\ldots(7)$$

§ 4. THE APPLICATION OF THE DEBYE THEORY

The formal theory quoted in the last section refers to the case of a single type of sound wave of constant velocity c. This differs from our case in two respects:

(*a*) It is an experimental fact that with decrease in temperature below the λ-point the velocity of first sound rises steadily with temperature,* and that of second sound rises rapidly from zero at the λ-point to a value which may be considered as roughly constant † between 2·0° K. and 1·03° K., the lowest temperature for which it has been measured. For a preliminary discussion we shall apply the results of the Debye theory as given above, replacing the temperature-dependent sound velocities by mean values. In §§ 8 and 9 of this paper a detailed treatment of this problem will be given; this yields information on the possible shape of the curve of second sound velocity against temperature.

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* Since the coefficient of expansion of helium II is both very small and negative, this holds for constant volume as well as for the measured results at constant pressure.

† More accurately, there is a very flat maximum in the curve of velocity against temperature at about 1·6° K. and a minimum at 1·12° K.

(*b*) The results of the last section have been given for the case of a single type of sound wave of velocity c. In our case we have two types of sound: first sound of velocity u_1, and second sound of velocity u_2. The question to be decided is that of allocating the $3N$ modes of vibration available. We may discuss the following simplifying assumptions: (i) The frequency limits are taken to be the same, in which case we may introduce a mean velocity c defined by the relation $1/c^3 = 1/u_1^3 + 1/u_2^3$, and then apply the theory given above without further alteration. We are assuming here that only longitudinal waves may pass through the liquid. (ii) The wavelength limits are taken to be the same, in which case we must take the frequency limits as proportional to the respective velocities. To preserve the total number of normal modes at $3N$, we must take the frequency limits as $\nu_1 = (9N/8\pi)^{\frac{1}{3}} u_1$ and $\nu_2 = (9N/8\pi)^{\frac{1}{3}} u_2$. We then consider the contributions from the two types of sound separately. In the known temperature region, where $u_2 \sim u_1/13$, the effects of first sound may be neglected, so that assumptions (i) and (ii) give the same result.

There is also a third possibility, which arises in the following way. In first sound our frequency limits are really connected with the point at which the concept of hydrodynamic flow becomes meaningless; this limit will be determined by the condition that the wavelength becomes of the order of magnitude of the interatomic distance. In second sound our frequency limit is determined by the breakdown of the concept of relative hydrodynamic flow between the superfluid and the normal fluid. This breakdown will occur when the wavelength is of the order of magnitude of the mean distance between superfluid atoms if these are in the minority, or between normal atoms if these are in the minority. We may then show that the characteristic temperature must be proportional to $(\rho_s/\rho)^{\frac{1}{3}}$ or to $(\rho_n/\rho)^{\frac{1}{3}}$, whichever is the smaller at the temperature considered. An objection to this argument must be raised. When we speak of a normal or a superfluid atom, we must remember that the chosen atom will remain "normal" or "superfluid" for a time of the order of the relaxation time between different energy states. If the relaxation time involved were much shorter than the reciprocal of the frequency of sound concerned, the above argument breaks down, as superfluid and normal atoms constantly interchange, so that we again become interested in the much more slowly varying mean distance between atoms, regardless of the energy levels which they occupy.

§ 5. COMPARISON WITH EXPERIMENT

A formally complete description of the thermodynamical behaviour of helium II should be given by the combination of the following equations. (The effects of first sound will be neglected, a procedure justified in the temperature region so far investigated.)

(1) The equation $u_2^2 = TS^2\rho_s/C\rho_n = (1-\rho/\rho_n)/d(1/S)/dT$.

(2) Equation (2) of § 3, or more accurately equation (11) of § 9, giving S in terms of u_2.

(3) The equation $\rho_n/\rho = 4E/3u_2^2$ (or more accurately equation (14) of § 9), an extension of an equation due to Landau (1941).

We have now sufficient equations to eliminate the unknowns—at least in principle. However, as has been remarked previously, it is much simpler to take the experimental values of u_2 or, alternatively, trial values, and check that they are consistent with these three equations and with the experimental values of the entropy.

First, it is instructive to calculate the entropy taking only first sound effects into account—i.e. to find the Debye entropy calculated according to previous theories. It is known that the velocity of first sound in helium II is about 240 metres per second, and that the molecular volume is 27·6 cm³. From these we deduce * the value $\theta_1 \sim 29^\circ$ K. from the relation $\theta_1 = \boldsymbol{h}\nu_m/\boldsymbol{k} = \boldsymbol{h}u_1(9N/4\pi)^{\frac{1}{3}}$. This value of the Debye characteristic temperature is so much higher than the temperatures in which we are interested that we may use the simple formulae valid in the T^3 region. The value of the entropy derived is $1{\cdot}8 \times 10^{-3}\, T^3$ cal/gm., which is to be compared with the experimental relation $S = 0{\cdot}405 \times (T/T_0)^{5{\cdot}5}$ cal/gm., T_0 being the temperature of the λ-point. Thus near the λ-point the experimental value of the specific heat ($T\,dS/dT$) is roughly 40 times the value calculated from the usual Debye theory, taking only first sound into account.

Let us now introduce second sound. At first sight it might appear that since $C \sim 1/c^3$ (in the T^3 region) and $u_2 \sim u_1/13$, second sound would contribute a specific heat about two thousand times as large as that of first sound. This is not so, because the introduction of second sound effects causes us to pass right out of the T^3 region for all except the very lowest temperatures. This may be seen from the relation $\theta \propto c$, showing that $\theta_2 \sim \theta_1/13 \sim 2{\cdot}2^\circ$ K., so that θ_2 is of the same order of magnitude as the temperatures we wish to consider. For instance, to take a very simple case, the energy is proportional to the integral $\int_0^{\theta/T} x^3\,dx/(e^x - 1)$ When $\theta/T \gg 1$ (i.e. in the T^3 region), this has the value 6·45, but when $\theta/T = 1$, say, it takes the value 0·224. Thus instead of second sound effects giving an energy approximately 2,000 times that previously calculated (assuming only first sound), it provides a contribution approximately 70 times as large. The other thermodynamical quantities are cut down in a similar way.

An experimental fact that is particularly interesting is that the specific heat just above the λ-point is unduly high, so much so that the slope of the curve of specific heat against temperature is negative. This may well imply that it is possible to transmit hypersonic waves of second sound at temperatures just above the λ-point; it may also be possible to transmit waves of attainable frequencies.

§6. THE THERMAL EXPANSION OF HELIUM II

Generally speaking, solids and liquids have a positive coefficient of thermal expansion. We wish to explain why the coefficient of thermal expansion of helium II is very small and negative in sign, whilst that of helium I is of normal magnitude and of normal (positive) sign. First we must find a quantitative relation between the coefficient of thermal expansion, α, say, and θ, the characteristic temperature. For the present we shall make the usual assumption that θ

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* Tisza (1947) has given the value 18° K., but we are unable to see how he arrives at this result. We also cannot agree with his criticism of Pickard and Simon's (1939) experimental value of θ, since the formulae for the specific heat, etc., given in terms of θ are completely independent of theoretical speculations concerning the existence or non-existence of transverse waves in liquids, these all being collected in the connection between θ and the velocity of sound.

depends only on volume—i.e. $\theta=\theta(V)$. Referring back to (2), we see that the entropy is a function of $T/\theta(V)$. Thus $S=S(T/\theta(V))$, so that

$$\left(\frac{\partial S}{\partial T}\right)_V=\frac{S'}{\theta} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T=-\frac{S'T}{\theta^2}\left(\frac{\partial \theta}{\partial V}\right)_T,$$

where S' is the differential coefficient of S with respect to the variable T/θ. Eliminating S', we have

$$\left(\frac{\partial S}{\partial V}\right)_T=-\left(\frac{T}{\theta}\right)\left(\frac{\partial \theta}{\partial V}\right)_T\left(\frac{\partial S}{\partial T}\right)_V.$$

Applying the Maxwell thermodynamic relationship $(\partial S/\partial V)_T=(\partial p/\partial T)_V$ and the relation $C=T(\partial S/\partial T)_V$ for the specific heat at constant volume, we obtain

$$\left(\frac{\partial p}{\partial T}\right)_V=-\frac{1}{\theta}\left(\frac{\partial \theta}{\partial V}\right)_T C=-\frac{\gamma C}{V},$$

where $\gamma=(\partial \ln \theta/\partial \ln V)_T$ and V is the molecular volume. Now since

$$dp=\left(\frac{\partial p}{\partial T}\right)_V dT+\left(\frac{\partial p}{\partial V}\right)_T dV,$$

we see that

$$\left(\frac{\partial p}{\partial T}\right)_V=-\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial V}\right)_T=\frac{\alpha}{\chi},$$

where α is the coefficient of thermal expansion and χ is the isothermal compressibility. Thus $\alpha=-\gamma C\chi/V$.

To sufficient accuracy we may treat χ and V as independent of temperature. It is worth noting that since α is proportional to C, the coefficient of expansion will have a peak value at the λ-point, and will fall to zero at very low temperatures.

The sign of the coefficient of expansion will be the same as the sign of $-\gamma$, i.e. the sign of $(-\partial c/\partial V)_T$, where c is the velocity of the hypersonic waves concerned. Above the λ-point we take $c=u_1$, the velocity of first sound; below the λ-point we may take with sufficient accuracy $c=u_2$, the velocity of second sound. In order to account for the observed behaviour of the expansion coefficient of helium, we must explain two points: (i) why $(\partial u_1/\partial V)_T$ above the λ-point is negative; (ii) why $(\partial u_2/\partial V)_T$ below the λ-point is very small and positive.

To explain (i) we recall the relation $u_1^2=\chi^*/\rho$, where χ^* is the adiabatic compressibility and ρ the density. Assuming the existence of short range forces, χ^* must depend on volume much more sensitively than ρ, so that the ratio will decrease with increase in volume.

To account for (ii), which has recently been checked experimentally, we recall the relation $u_2^2=(1-\rho/\rho_n)/d(1/S)/dT$. It is unlikely that either the fraction of normal fluid ρ_n/ρ or the entropy per unit mass would be sensitive to volume changes, so that a very small value of $(\partial u_2/\partial V)_T$ is to be expected. Quantitatively, we may investigate the magnitude of $(\partial u_2/\partial V)_T$ by finding a relation between the change in velocity due to alterations in volume and the change in velocity due to variations in temperature. Let us write $f=u_2/T^{\frac{1}{2}}=(S^2\rho_s/C\rho_n)^{\frac{1}{2}}$, so that f depends only on the quantities which will be given by a theory of the Debye type, $f=f(T/\theta)$. The λ-point T_0 is given by the condition that all atoms are normal, i.e. by $\rho_n(T_0)=\rho$. We have seen that $\rho_n \propto E/u_2^2$. Hence T_0 will be given linearly in terms of θ, and, therefore, $f=f(T/T_0)$. Thus $(\partial f/\partial T_0)=-(T/T_0)(\partial f/\partial T)$ and hence

$$\left(\frac{\partial f}{\partial V}\right)_T=-\frac{T}{V}\left(\frac{d\ln T_0}{d\ln V}\right)_T\left(\frac{\partial f}{\partial T}\right)_V.$$

The slope of the λ-line in the p, T diagram of helium is negative, so that $(d \ln T_0/d \ln V)_T$ is positive, although very small. The sign of $(\partial f/\partial T)_V$, i.e. the slope of the curve of $u_2/T^{\frac{1}{2}}$ against temperature, is found to be negative in the temperature region so far investigated. Hence $(\partial u_2/\partial V)_T = T^{\frac{1}{2}}(\partial f/\partial V)_T$ will be very small and positive, as required to explain (ii). In principle, this argument might be extended by the methods of § 5, so as to become independent of experimental values of velocity.

§ 7. THE ORDINARY THERMAL CONDUCTIVITY AND THE ATTENUATION OF SECOND SOUND

Debye (1914) and Brillouin (1914, 1920) have suggested a theory giving the coefficient of thermal conductivity of solids (and liquids) in terms of the velocity and attenuation of the hypersonic waves of sound supposed present. The theory is analogous to the well-known one for the thermal conductivity of a gas, i.e. that leading to the result $K = \frac{1}{3}mCnlc$, where m is the mass of a gas molecule, n the number of gas molecules per unit volume, C the specific heat per gramme, l the mean free path of a molecule and c the mean velocity of the molecules. $(mCn\delta T)$ is the heat transported across a temperature difference δT by the molecules contained in a unit volume; the analogous quantity in the wave picture of a solid or liquid will be

$$\frac{\partial}{\partial T}\left(\frac{4\pi\nu^2}{c^3}\,\frac{\boldsymbol{h}\nu}{\exp(\boldsymbol{h}\nu/\boldsymbol{k}T)-1}\right)\delta T$$

per unit frequency range, since the bracketed expression is the thermal energy per unit volume at temperature T. In the wave picture l will now refer to the mean free path of a wave—i.e. to the reciprocal of the attenuation coefficient of the sound waves concerned, and c will refer to the mean velocity of these waves. Integrating over all frequencies, we find for the coefficient of thermal conductivity the expression

$$K = \tfrac{1}{3}c\int_0^{\nu_{\mathrm{m}}} l\,\frac{\partial}{\partial T}\left(\frac{4\pi\nu^2}{c^3}\,\frac{\boldsymbol{h}\nu}{\exp(\boldsymbol{h}\nu/\boldsymbol{k}T)-1}\right)d\nu.$$

For the ideal case in which c, ν_{m} and l are independent of temperature this reduces to

$$K = \tfrac{1}{3}cl\,\frac{\partial}{\partial T}\int_0^{\nu_{\mathrm{m}}}\frac{4\pi\nu^2}{c^3}\,\frac{\boldsymbol{h}\nu}{\exp(\boldsymbol{h}\nu/\boldsymbol{k}T)-1}\,d\nu = \tfrac{1}{3}\rho clC,$$

where C is the specific heat per unit mass. This ideal relation is the same for solids, liquids and gases, provided the symbols are interpreted in the appropriate manner.

For the case of liquid helium we have $K = \frac{1}{3}\rho(l_1u_1C_1 + l_2u_2C_2)$, where C_1 and C_2 are the contributions to the specific heat from first and second sound respectively. As we have seen, below the λ-point $u_2C_2 \gg u_1C_1$, whilst above $u_2\,C_2 = 0$, so that we have

$$K \simeq \tfrac{1}{3}\rho l_2 u_2 C(T) \text{ for } 0 < T < \lambda\text{-point}, \qquad K = \tfrac{1}{3}\rho l_1 u_1 C(T) \text{ for } T > \lambda\text{-point}.$$

The value of the product uC does not vary by more than an order of magnitude for liquid helium over the greater part of its temperature range. This is due to a series of compensating effects. For instance, the large value of the specific heat just below the λ-point is compensated by a fall in the velocity of second sound, and the change over to the value of the velocity of first sound is compensated by the fact that the specific heat just above the λ-point is much smaller than that just below it. Thus any striking variation in K would be due to a change in the attenuation.

We must stress the fact that K is the ordinary thermal conductivity, i.e. the heat flux per unit temperature gradient. As has been shown (Dingle 1948), a finite value for K will result in absorption of second sound by irreversible processes. If we assume that the attenuation due to this cause is of prime importance, we may find l and K explicitly by combining the results of this section with a result of the previous paper, i.e. $l_2 = 2u_2^3\rho C/K\omega^2$, where u_2, ρ, C and K refer respectively to the velocity of second sound, the fluid density, the specific heat per unit mass and the ordinary conductivity, and $\omega/2\pi$ is the frequency. This expression shows that the mean free path is in fact a function of the frequency ν. Strictly speaking, therefore, we are unable to use the simplified expressions giving K in terms of l, except for rough estimates. We may show very simply that the theory gives reasonable value for K and l. The minimum free path l_{min} will be that for the waves of highest frequency ν_{m}. Thus

$$l_{\text{min}} \sim 8\pi^2 u_2^3 \rho C/K\nu_{\text{m}}^2 \quad \text{and} \quad K \sim \tfrac{1}{3}\rho l_{\text{min}} u_2 C$$

giving

$$K \sim (8\pi^2/3)^{\frac{1}{2}} \rho u_2^2 C/\nu_{\text{m}} = (8\pi^2/3)^{\frac{1}{2}} \boldsymbol{h}\rho u_2^2 C/\boldsymbol{k}\theta,$$

and

$$l_{\text{min}} \sim (24)^{\frac{1}{2}} \pi u_2/\nu_{\text{m}} = (24)^{\frac{1}{2}} \boldsymbol{h} u_2/\boldsymbol{k}\theta.$$

Numerically, $l_{\text{min}} \sim 7 \times 10^{-7}$ cm. at 1·5° K. This is a satisfactory value, showing that the minimum free path is of the order of twenty interatomic distances. A smaller value would have shown that the maximum frequency of vibration is dictated not by the number of normal modes available, but by absorption effects.

We may proceed further and determine the approximate mean free path of second sound waves of attainable frequencies. Since $l(\nu) \propto 1/\nu^2$ for a given temperature, we have $l(\nu) \sim 7 \times 10^{-7}(\nu_{\text{m}}/\nu)^2$ at 1·5° K., where $\nu_{\text{m}} \sim 4 \times 10^{10}$ cycles per second.

§ 8. THE DEBYE THEORY AND THE NECESSITY FOR MODIFICATION

In this section we wish to show that the use of the ordinary Debye theory is not justified if the sound velocities (at constant volume) vary with temperature.

The number of independent modes of vibration per unit volume is known to be $4\pi\nu^2/c^3$ per unit frequency range, where c is a velocity of sound. We shall find it convenient to rewrite this expression. Let p be the momentum of a wave, then the energy is given by $\epsilon = pc = \boldsymbol{h}\nu$, so that the number of modes per unit volume is given by $4\pi p^2/\boldsymbol{h}^3$ per unit momentum range. The upper limit to this momentum, p_{m} say, is given by the consideration that the number of modes per unit volume is $3N$, where N is the number of atoms per unit volume. Thus $3N = (4\pi/\boldsymbol{h}^3)\int_0^{p_{\text{m}}} p^2\,dp$, and hence $p_{\text{m}} = (9N\boldsymbol{h}^3/4\pi)^{\frac{1}{3}}$. Therefore p_{m} is independent of temperature. However, the energy of each wave of given momentum, $\epsilon = pc$, may not be constant, since the velocity c may vary with temperature. Supposing for the present that this variation of the velocity is negligible, we have for the partition function $Z = \Pi_i\{1 - \exp(p_i c/\boldsymbol{k}T)\}^{-1}$, where p_i are the allowed momenta, this being the well known result valid for a set of oscillators with no restriction either on the number of quanta allowed per oscillator or the number allowed per energy level.

We may proceed in two ways: either we may work out the free energy $A = -\boldsymbol{k}T \ln Z$ and from this the thermodynamic quantities, or else we may find the mean occupation numbers $\bar{n}_i$ from the relation $\bar{n}_i = z_i \partial \ln Z/\partial z_i$, where

$z_i = \exp(-p_i c/\boldsymbol{k}T)$, and from these the mean energy, and hence, by differentiation, the specific heat. Using the former method, and still supposing the temperature variation of the velocity to be negligible, we have

$$A = -\boldsymbol{k}T \ln Z = \boldsymbol{k}T \Sigma_i \ln\{1 - \exp(-p_i c/\boldsymbol{k}T)\}$$

$$= \boldsymbol{k}T \frac{4\pi}{\boldsymbol{h}^3} \int_0^{p_{\mathrm{m}}} p^2\, dp \ln\{1 - \exp(-pc/\boldsymbol{k}T)\}.$$

Introducing the Debye characteristic temperature θ by the relation $\boldsymbol{k}\theta = p_{\mathrm{m}} c$, we obtain

$$\frac{A}{T} = 9R\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} x^2\, dx \ln(1 - e^{-x}) = 3R\left[\ln(1 - e^{-\theta/T}) - \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3\, dx}{e^x - 1}\right] \qquad \ldots\ldots(8)$$

per molecular volume. Using the well-known thermodynamic formulae for the entropy S, the energy E, and the specific heat C, viz. $S = (E - A)/T = -(\partial A/\partial T)_V$ and $E = -T^2[\partial(A/T)/\partial T]_V$ (from the Gibbs-Helmholtz equation), and

$$C = -T(\partial^2 A/\partial T^2)_V = \partial E/\partial T,$$

we deduce equations (1), (2) and (3) of § 3.

Combining (8) with the relationship $p = -(\partial A/\partial V)_T$, we find the equation of state

$$p + dW/dV = -E[\partial \ln \theta/\partial V]_T, \qquad \ldots\ldots(9)$$

where W is the energy at the absolute zero.

Using the second method, that involving occupation numbers, we have

$$\bar{n}_i = z_i \partial \ln Z/\partial z_i = 1/\{\exp(p_i c/\boldsymbol{k}T) - 1\},$$

so that $\epsilon_i = p_i c/\{\exp(p_i c/\boldsymbol{k}T) - 1\}$, and, therefore,

$$E = \frac{4\pi}{\boldsymbol{h}^3} \int_0^{p_{\mathrm{m}}} \frac{(pc)p^2\, dp}{\exp(pc/\boldsymbol{k}T) - 1} = 9RT\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3\, dx}{e^x - 1},$$

which is the same as the expression deduced by the first method. It is clear, however, that the two methods would yield quite different results if we took into account the variation of the velocity with temperature, for then the value of E given by the second method would be unchanged, since no differentiations with respect to temperature are involved, whilst the energy derived by the first method would be different.

§ 9. TEMPERATURE-DEPENDENT DISTRIBUTIONS OF ENERGY LEVELS

The difficulty pointed out in § 8 is caused by the fact that the energy levels which we are considering are themselves functions of temperature. This may be seen from the energy relation $\epsilon = pc$, where p may be considered as independent of temperature, since we must integrate over all values of p up to a maximum value p_{m} which is independent of temperature. The concept of temperature-dependent energy levels arises only because of the difficulties of a complete treatment by the methods of statistical mechanics. If we included in the partition function every possible arrangement of the system, temperature-dependent energy levels would never arise. However, in many problems which are treated approximately, temperature-dependent energy levels are bound to be the rule. It is known in several special cases in classical statistical mechanics (or rather quantum statistical mechanics at higher temperatures) that the correct procedure is to replace the energies in the exponential terms by free energies. Rushbrooke (1940) has considered this problem in more detail, and has pointed out that we obtain agreement between statistical mechanics and thermodynamics by this procedure in any case in which, in the notation of his paper, $\overline{N}=\lambda(\partial/\partial\lambda)\ln G(\lambda\theta^{\varepsilon})$ and $\overline{E}=\theta(\partial/\partial\theta)\ln G(\lambda\theta^{\varepsilon})$, where $\ln\theta=-1/\boldsymbol{k}T$ and G is a generating function: λ is found by equating the sums of terms such as $\overline{N}$ to the total number of systems in the assembly, and θ by equating the sum of terms such as $\overline{E}$ to the total energy of the assembly. This is equivalent to the statement that the procedure of replacing the energy by the free energy in the exponential terms is justified for all cases in which the method of steepest descents is applicable to the contour integral appearing in the evaluation of the partition function. That the procedure is one of great generality is shown by the following demonstration.

In the customary theory, the partition function is taken to be

$$Z=\Sigma\exp[-\Sigma_i n_i\epsilon_i/\boldsymbol{k}T],$$

where the ϵ_i designate the energy levels and n_i the occupation numbers. The outer summation is carried out over all possible configurations (e.g. in the case of a fixed number of particles, N say, this is subject to the condition that $\Sigma_i n_i=N$), and the inner summation according to all configurations consistent with the particular statistics employed. Let us replace this formally by $Z=\Sigma\exp[-\Sigma_i n_i f_i/\boldsymbol{k}T]$. From the Gibbs-Helmholtz equation $A-E=T(\partial A/\partial T)_V$, where A is the free energy, we obtain $E=-T^2[\partial(A/T)/\partial T]_V$. By definition, $A=-\boldsymbol{k}T\ln Z$, so that

$$E=\boldsymbol{k}T^2\left(\frac{\partial\ln Z}{\partial T}\right)_V=\frac{\Sigma[\Sigma_i n_i\{f_i-T(\partial f_i/\partial T)_V\}]\exp[-\Sigma_i n_i f_i/\boldsymbol{k}T]}{\Sigma\exp[-\Sigma_i n_i f_i/\boldsymbol{k}T]}.$$

Clearly we must have $$E=\frac{\Sigma[\Sigma_i n_i\epsilon_i]\exp[-\Sigma_i n_i f_i/\boldsymbol{k}T]}{\Sigma\exp[-\Sigma_i n_i f_i/\boldsymbol{k}T]},$$

since E is merely the energy of each configuration, $\Sigma_i n_i\epsilon_i$, averaged over all possible configurations. Hence, in general,

$$\epsilon_i=f_i-T(\partial f_i/\partial T)_V$$

which is the Gibbs-Helmholtz equation for the energy levels, provided the f_i are interpreted as free energies.

This result may easily be confirmed for the particular partition function in which we are interested, i.e. $Z=\Pi_i\{1-\exp(-f_i/\boldsymbol{k}T)\}^{-1}$.

The effective free energy of a sound wave may be found from the expression $\epsilon=pc(T)$. From the Gibbs-Helmholtz equation, $f-T(\partial f/\partial T)_V=\epsilon$, we have $[\partial(f/T)/\partial T]_V=\epsilon/T^2$ and thus $f=T\int_T^{T_0}(\epsilon/T^2)\,dT$, where the upper limit T_0 is left undefined. In the sequel we shall simply write c for $[c(T)]_V$.

We take for the logarithm of the partition function the expression

$$\ln Z=-\frac{4\pi}{\boldsymbol{h}^3}\int_0^{p_{\mathrm{m}}}p^2\,dp\ln\left[1-\exp\left\{-\frac{p}{\boldsymbol{k}}\int_T^{T_0}(c/T^2)\,dT\right\}\right],$$

where $p_{\mathrm{m}}=\boldsymbol{h}(9N/4\pi)^{\frac{1}{3}}$. For convenience we put $x=(p/\boldsymbol{k})\int_T^{T_0}(c/T^2)\,dT$, so that $x_{\mathrm{m}}=\frac{h}{\boldsymbol{k}}\left(\frac{9N}{4\pi}\right)^{\frac{1}{3}}\int_T^{T_0}\frac{c}{T^2}\,dT$. Then $\ln Z=-\frac{9N}{x_{\mathrm{m}}^3}\int_0^{x_{\mathrm{m}}}x^2\,dx\ln(1-e^{-x})$ and thus

$$\frac{A}{T}=-\boldsymbol{k}\ln Z=\frac{9R}{x_{\mathrm{m}}^3}\int_0^{x_{\mathrm{m}}}x^2\,dx\ln(1-e^{-x})=3R\left[\ln(1-e^{-x_{\mathrm{m}}})-\frac{1}{x_{\mathrm{m}}^3}\int_0^{x_{\mathrm{m}}}\frac{x^3\,dx}{e^x-1}\right] \qquad \ldots\ldots(9)$$

per molecular volume. The energy E may be obtained either directly, thus

$$E=\frac{4\pi}{\boldsymbol{h}^3}\int_0^{p_{\mathrm{m}}}\frac{(pc)p^2\,dp}{\exp\left[(p/\boldsymbol{k})\int_T^{T_0}(c/T^2)\,dT\right]-1}=\frac{9Rc}{\int_T^{T_0}(c/T^2)\,dT}\,\frac{1}{x_{\mathrm{m}}^3}\int_0^{x_{\mathrm{m}}}\frac{x^3\,dx}{e^x-1}, \qquad \ldots\ldots(10)$$

or from A/T by differentiation, noting that

$$\frac{1}{x_{\mathrm{m}}}\frac{\partial x_{\mathrm{m}}}{\partial T}=-\frac{c/T^2}{\int_T^{T_0}(c/T^2)\,dT}.$$

The solutions given by the two methods now agree.

The entropy may be found either by using the thermodynamic definition $A=E-TS$, giving

$$S=\frac{E-A}{T}=3R\left[\ln(1-e^{-x_{\mathrm{m}}})+\frac{1}{x_{\mathrm{m}}^3}\int_0^{x_{\mathrm{m}}}\frac{x^3\,dx}{e^x-1}\left\{1+\frac{3c}{T\int_T^{T_0}(c/T^2)\,dT}\right\}\right] \qquad \ldots\ldots(11)$$

or from the thermodynamic formula $S=-(\partial A/\partial T)_V$. There is no need to verify that we obtain the same result, since by elimination of S between these two expressions, i.e. $S=(E-A)/T=-(\partial A/\partial T)_V$, we return to the Gibbs-Helmholtz equation which was used in the derivation of the energy: the two values of S are therefore bound to be identical. Finally, the specific heat C may be found either by differentiation of the energy, or of the entropy, i.e. $C=\partial E/\partial T=T(\partial S/\partial T)_V$. By either method we obtain

$$C=9R\left[\frac{1}{x_{\mathrm{m}}^3}\int_0^{x_{\mathrm{m}}}\frac{x^2\,dx}{e^x-1}\left\{4\left(\frac{c}{T\int_T^{T_0}(c/T^2)\,dT}\right)^2+\frac{\partial c/\partial T}{\int_T^{T_0}(c/T^2)\,dT}\right\}\right.$$
$$\left.-\left(\frac{c}{T\int_T^{T_0}(c/T^2)\,dT}\right)^2\left(\frac{x_{\mathrm{m}}}{e^{x_{\mathrm{m}}}-1}\right)\right]. \qquad \ldots\ldots(12)$$

In a similar way, we may show that the equation of state is now

$$p+\frac{dW}{dV}=-E\left(\frac{\partial\ln x_{\mathrm{m}}}{\partial V}\right)_T\frac{T\int_T^{T_0}(c/T^2)\,dT}{c} \qquad \ldots\ldots(13)$$

and that the equation ρ_{n}/ρ should now read

$$\rho_{\mathrm{n}}/\rho=\frac{4}{3}\,\frac{E}{cT\int_T^{T_0}(c/T^2)\,dT}. \qquad \ldots\ldots(14)$$

The theory given above leaves undetermined the upper limit T_0 of the integrals involved. In our case three choices might be made: (i) $T_0=0°$ K.; in this case we must assume that $c(T)$ varies in such a way that the integrals do not diverge at extremely low temperatures, i.e. near $T=0$, $c(T)\propto T^n$, where $n>1$; (ii) $T_0=2{\cdot}19°$ K., the λ-point; (iii) $T_0=\infty$.

The second and third give the same result, since $u_2=0$ for $T\geqslant 2{\cdot}19°$ K. However, the integrals would have a zero value at the λ-point, which would lead to difficulties—for instance, infinities would appear unless the attenuation of the sound were taken into account in detail. It is therefore probable that $T_0 = 0^\circ$ K., predicting a zero value for the velocity of second sound at the absolute zero.

Note added in proof. Recent Experimental Work.

Peshkov (1948a) has recently made measurements of the velocity of second sound at lower temperatures than those used in previous experiments. These show that the velocity again rises at temperatures lower than $1{\cdot}12^\circ$ K., in accordance with Landau's prediction (Landau 1941, Dingle 1948, § 11). Thus the mean value of θ_2 will be greater than that estimated in § 5 of the present paper. As a result, the values of the thermodynamical quantities will be reduced, leading to better agreement between theory and experiment.

Peshkov (1948b) has also measured the velocity of second sound as a function of pressure, i. e. $(\partial u_2/\partial p)_T$. This he finds to be small and negative, so that $(\partial u_2\ \partial V)_T$ will be small and positive, as predicted theoretically in § 6 of this paper. Quantitatively, by similar arguments to those of § 6, we obtain

$$\left(\frac{\partial u_2}{\partial p}\right)_T = \frac{T^{3/2}}{T_0}\frac{dT_0}{dp}\cdot\left(\frac{\partial(u_2/\sqrt{T})}{\partial T}\right)_p.$$

This relation yields values of $(\partial u_2/\partial p)_T$ in close agreement with Peshkov's experimental results for temperatures near the λ-point—i. e. in the temperature region in which u_2 varies rapidly with temperature. For temperatures in the neighbourhood of the maximum of $u_2(T)$ it gives values which are too small by a factor of about four. It follows from the above relation that $-(\partial u_2/\partial p)_T$ should again rise in value for temperatures lower than $1{\cdot}12^\circ$ K.

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The Surface Energies of Inert-gas and Ionic Crystals

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ABSTRACT. It is shown that the surface energies of inert-gas crystals are proportional to their sublimation energies. The constant of proportionality is evaluated for the {111}, {100} and {110} faces for different assumed forms of the interatomic repulsive forces; to within 15% it is independent of the face, and of the form of the repulsive force. The distance of the outermost plane of atoms from the next at a {100} face is 2·54% greater than normal; this distortion makes a negative contribution of 1% to the surface energy.

The surface energies of sodium and potassium halide crystals are calculated; the ratio of the energies of {110} and {100} faces is about 2·5. The contribution of van der Waals type forces to the surface energy of a {100} face is almost half the total.

Elementary methods are given for the evaluation of lattice sums.

§ 1. INTRODUCTION

The total free energy of a volume of liquid is the sum of two terms, one proportional to the volume, the other to the surface area; the surface free energy per unit area is defined as the proportionality factor in the second term. The surface free energy per unit area of a crystal face is similarly defined, having regard to the fact that different faces of a crystal have different energies.

Both the surface free energy and the surface "internal" energy are difficult to calculate because they depend on the thermal vibrations. The surface energy at 0° K. is a simpler quantity, for except for zero-point vibrations the molecules are at rest. If the molecules can be regarded as acting upon each other with forces that depend only upon their separation, then the surface energy at 0° K. is the excess potential energy of molecules near the surface.

An increase in area of a given volume of material can occur by its division into two parts by a plane, and the separation of these parts to an infinite distance. This can be supposed to occur in two stages and the energy change of each stage can be calculated. In the first stage the molecules of each part are supposed held in their original relative positions by constraints, so that the energy per unit area needed to separate these two parts to infinity is $2U_0'$, where $-2U_0'$ was the mutual potential per unit area between the two parts before separation. In the second stage the constraints on the molecules are relaxed, the surface molecules are no longer in equilibrium and move to a position of lower energy; this reduces the energy of each surface by an amount U_0'' per unit area. Thus the surface energy per unit area at 0° K. is

$$U_0 = U_0' - U_0''. \qquad \qquad ......(1)$$

U_0'' is a small correction to U_0'.

Numerous authors have attempted to calculate U_0' for homopolar liquids on the assumptions that the forces between any two molecules act along their line of centres, are independent of the presence of other molecules, and depend only on their distance apart, i.e. they are central and additive. Using these assumptions Gauss (see for example Rayleigh (1890) or Fowler and Guggenheim (1939)) treated a liquid as a continuum and obtained the expression

$$U_0' = -\tfrac{1}{2}\pi n^2 \int_0^{\infty} r^3 \epsilon(r)\, dr, \qquad \ldots\ldots(2)$$

where $\epsilon(r)$ is the potential between two molecules at a distance r apart and n is the number of molecules per unit volume. This gives correctly the contribution to U_0' of those molecules distant from the plane of section.* It shows that if $\epsilon(r)$ decreases less rapidly than r^{-4} the integral does not converge, and then the concept of a constant surface energy per unit area independent of size is not valid. If a volume is so large that gravitational forces between the molecules affect capillary phenomena, they must be estimated independently.

If, however, $\epsilon(r)$ contains terms that, at $r=0$, change more rapidly than r^{-4}, the integral (2) diverges at the lower limit. Edser (1922), Bakker (1928), Bradley (1931), Kassel and Muscat (1932) and Belton and Evans (1941) have avoided this divergence by using the atomic diameter as the lower limit; this is quite arbitrary and introduces very large and unpredictable errors.

To obtain an accurate estimate of U_0' it is not sufficient to treat a liquid as a continuum; a knowledge of the molecular arrangement is necessary. Jura (1948) used the experimentally determined radial distribution function of argon and calculated $U'_{\text{M.P.}}$, the surface potential energy of the liquid at the melting point, from a generalization of equation (2). He assumed that the distribution of atoms near the surface is not altered by the presence of the surface. This procedure is somewhat tedious and demands a knowledge of the radial distribution function.

In this paper it is shown that for a homopolar substance, either liquid or solid, in which the interatomic forces are central and additive,

$$U_0 = K\epsilon_0/a_0^2, \qquad \ldots\ldots(3)$$

where ϵ_0 is the heat of evaporation and a_0 is a characteristic interatomic distance; both quantities are supposed extrapolated to 0° K. The value of K depends on the form of the interatomic force, $\epsilon(r)$, and upon the molecular arrangement. Values of K for $\{111\}$, $\{100\}$, $\{110\}$ faces of face-centred-cubic crystals and for different interatomic repulsive forces are calculated by a method of lattice sums devised by Born and Stern (1919) for ionic crystals. The theory is applied to inert-gas atoms, for which the assumptions are most likely to be valid.

Calculations of the surface energies of the $\{100\}$ and $\{110\}$ faces of sodium and potassium halides have been made by Born and Stern (1919), Lennard-Jones and Taylor (1925), and Dent (1929). However, doubt has been thrown on these results because they were less than half the observed value for the liquid. It is shown that this discrepancy is largely due to the neglect of van der Waals attractive forces, which in these ionic salts make a large contribution to the surface energy.

No reliable measurements have been made of the surface energies of solids and it is necessary to compare the theoretical results with the observed values for the liquids. Exact agreement is not to be expected because of the different molecular arrangement in solids and liquids, especially at the surface.

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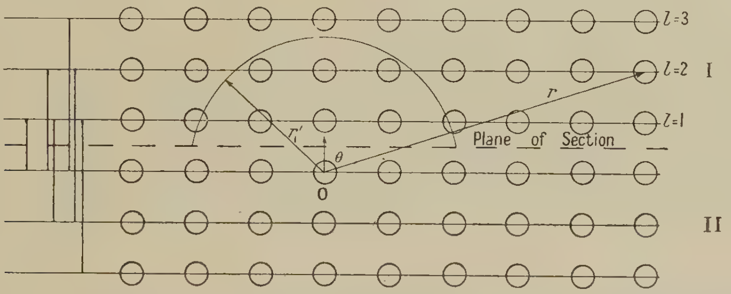
* The contributions of distant molecules to U_0' are found by multiplying I of equation (30) by $-\tfrac{1}{2}hn$; for a continuum $h \to 0$ and the second integral vanishes.

§ 2. THE MUTUAL POTENTIAL BETWEEN TWO PARTS OF A CRYSTAL

It is necessary to calculate the mutual potential per unit area between two parts of a homopolar crystal separated by an imaginary plane of section. Because of the regular crystal structure all atoms can be regarded as lying on planes parallel to the plane of section, and when all lattice points are equivalent the separation h between all adjacent planes is the same. The mutual potential between the two parts, I and II of the crystals (see Figure), is the sum of the potentials between all planes in part I and all planes in part II. The potential between any two such parallel planes depends only upon their separation.



From the Figure it is seen that in the expression for the mutual potential the contribution of a pair of planes at separation h occurs once, at separation $2h$ twice, and so on. If the planes in part I be enumerated $l=1, 2, 3, \ldots$, then the mutual potential (per atom in the surface plane) $-2u_0'$, is

$$-2u_0' = \sum_{l \geqslant 1} l\epsilon(r). \qquad \ldots\ldots(4)$$

Here u_0' is the surface energy per atom in the surface plane, r is the distance between an atom O in the surface plane ($l=0$) of part II and an atom in the plane l of part I; the summation is over all atoms in part I.

This method of calculating the surface energy is based on the assumptions that the interatomic forces are central and additive; these are valid only for inert-gas and ionic crystals. In inert-gas crystals the attractive forces between atoms are van der Waals, which London (1937) showed to be additive. The attractive forces between the ions of ionic crystals are van der Waals and electrostatic forces; the latter are clearly both central and additive. For neither inert-gas nor ionic crystals is it certain that the repulsive forces are additive, but this will be assumed for the inert-gas crystals; for ionic crystals only repulsive forces between nearest and next-nearest neighbour ions will be considered. The form of this assumption is not important because it affects only the interaction between atoms which are not nearest neighbours, and this is small because the forces decrease rapidly with distance.

The method of calculation is not appropriate to metals for which the surface energy is best regarded as arising from the change in kinetic energy of the free electrons due to the presence of the surface (Huang and Wyllie 1949). Nor can it be applied immediately to molecules with a permanent dipole moment, for these will be oriented at the surface of the liquid, and this will give rise to large values of U_0''. For covalent crystals, such as diamond, the best model is perhaps that of Harkins (1942) who considered only forces between nearest-neighbour atoms; this leads to a simple expression for K.

§3. THE SURFACE ENERGIES OF INERT-GAS CRYSTALS

(i) *Calculation of* U_0'

The force between two atoms is attractive at large distances and repulsive at small distances; at intermediate distances there is an equilibrium separation where the potential energy is a minimum. A simple expression that shows this behaviour is

$$\epsilon(r)=\lambda r^{-s}-\mu r^{-t} \quad s>t, \qquad \ldots\ldots(5)$$

where $\epsilon(r)$ is the potential between two atoms a distance r apart; $-s\lambda r^{-(s+1)}$ can be regarded as the short range repulsive force and $t\mu r^{-(t+1)}$ the longer range attractive force. From a knowledge of $\epsilon(r)$ both u_0' and u_0'' can be calculated.

The lattice of inert-gas crystals is face-centred cubic; this may be regarded as a simple cubic lattice, of lattice constant a_0, in which only alternate sites are occupied. Taking coordinate axes parallel to the cube axes, the coordinates of an atom, with respect to another, are $(m_1a_0,\ m_2a_0,\ m_3a_0)$ where m_1, m_2, m_3 are integers (positive, negative or zero) such that $m_1+m_2+m_3$ is even. Combining equations (4) and (5)

$$-2u_0'=\lambda a_0^{-s}\left[\sum_{\substack{l\geqslant 1\\ m_1+m_2+m_3\ \text{even}}}\frac{l}{(m_1^2+m_2^2+m_3^2)^{s/2}}\right]$$

$$-\mu a_0^{-t}\left[\sum_{\substack{l\geqslant 1\\ m_1+m_2+m_3\ \text{even}}}\frac{l}{(m_1^2+m_2^2+m_3^2)^{t/2}}\right], \qquad \ldots\ldots(6)$$

$$-2u_0'=B_s''\lambda a_0^{-s}-B_t''\mu a_0^{-t}. \qquad \ldots\ldots(7)$$

Numerical values of the lattice sums B'' and details of their computation are given in the Appendix for {111}, {110}, and {110} planes for powers between 6 and 12.

Instead of using explicit values of the force constants λ and μ it is possible to express u_0' in terms of the heat of sublimation of the crystal. The mutual potential of an atom in the centre of a crystal with respect to all the other atoms is

$$-2\epsilon_0=\Sigma\epsilon(r), \qquad \ldots\ldots(8)$$

where ϵ_0 is the heat of sublimation per atom at 0° K. (corrected for zero point vibrations) and the summation is over all the other atoms. The factor 2 occurs because when the sum is repeated for every atom as origin the interaction of each pair is counted twice. Using equation (5)

$$-2\epsilon_0=\lambda a_0^{-s}\left[\sum_{m_1+m_2+m_3\ \text{even}}\frac{1}{(m_1^2+m_2^2+m_3^2)^{s/2}}\right]$$

$$-\mu a_0^{-t}\left[\sum_{m_1+m_2+m_3\ \text{even}}\frac{1}{(m_1^2+m_2^2+m_3^2)^{t/2}}\right], \qquad \ldots\ldots(9)$$

$$-2\epsilon_0=A_s''\lambda a_0^{-s}-A_t''\mu a_0^{-t}. \qquad \ldots\ldots(10)$$

Lennard-Jones and Ingham (1925) have evaluated A'' for powers between 4 and 30. At 0° K. the lattice potential energy ϵ_0 is a minimum with respect to variations in a.

$$sA_s''\lambda a_0^{-s}=tA_t''\mu a_0^{-t}. \qquad \ldots\ldots(11)$$

Eliminating λa_0^{-s} and μa_0^{-t} from equations (7), (10), (11),

$$u_0'=\frac{sB_t''/A_t''-tB_s''/A_s''}{s-t}\epsilon_0=k(s,t)\epsilon_0. \qquad \ldots\ldots(12)$$

The attractive forces between inert-gas atoms are van der Waals type, for which $t=6$. In Table 1, $k(s,6)$ for a $\{111\}$ plane is tabulated for values of s between 7 and infinity. Increasing values of s correspond to increasing "hardness" of the atoms; when s is infinite the atomic model is that of rigid spheres with attractive forces.

Table 1. Variation of ${}_{111}k$ with "Hardness" of the Atoms

s	7	8	9	10	11	12	∞
${}_{111}k(s,6)$	0·502	0·450	0·418	0·398	0·384	0·374	0·313

If the interaction between atoms that are not nearest neighbours is neglected, then B_t''/A_t'' and B_s''/A_s'' are each equal to the ratio of the number of nearest neighbours in the plane $l=1$ (3), to the total number of nearest neighbours, (12); k is then $\frac{1}{4}$.

The most significant basis of comparison for the surface energies of different crystal faces is the energy per unit area U_0'

$$ {}_{\mathrm{P}}U_0' = {}_{\mathrm{P}}u_0'/\omega_{\mathrm{P}}a_0^2 = {}_{\mathrm{P}}K(s,t)\epsilon_0/a_0^2, \qquad \ldots\ldots(13)$$

where $1/\omega_{\mathrm{P}}a_0^2$ is the number of atoms per unit area in the surface plane of crystal face $\{\mathrm{P}\}$. In Table 2 values of ${}_{\mathrm{P}}K(s,6)$ are tabulated for $\{111\}$, $\{100\}$, and $\{110\}$ planes for s between 7 and infinity.

Table 2. Variation of K with Crystal Face and "Hardness" of the Atoms

s	7	8	9	10	11	12	∞
${}_{111}K(s,6)$	0·290	0·260	0·242	0·230	0·222	0·216	0·181
${}_{100}K(s,6)$	0·292	0·264	0·247	0·236	0·229	0·224	0·196
${}_{110}K(s,6)$	0·301	0·273	0·257	0·247	0·240	0·235	0·206

The variation of surface energy with crystal face arises from the different arrangement of the atoms that are near the surface; the contribution to ${}_{\mathrm{P}}U_0'$ of atoms distant from the plane of section is the same for all faces. The greater the relative importance of the interaction between neighbouring atoms the greater is the variation of surface energy with crystal face; thus the variation increases with increase of s and t. Yamada (1923, 1924) and Frenkel (1945) have shown that the surface energy per unit area of a crystal changes continuously with change of orientation of a crystal face, and that faces with large indices need not necessarily have large energies. This is because faces with large indices can be regarded as a series of steps formed from planes of low indices and of height equal to the interplanar separation. When such steps are few in number the increase in surface energy is only slight. Thus for a homopolar face-centred-cubic crystal the $\{110\}$ and $\{111\}$ faces have the absolute maximum and minimum surface energies per unit area; for an inert-gas crystal they do not differ by more than 10%.

From a knowledge of the heat of sublimation and the lattice constant of an inert-gas crystal it is possible to calculate the surface energy to within 15%; a more accurate estimate demands a knowledge of s. Values of s are derived from the variation of the second virial coefficient of the gas with temperature; Buckingham (1938) has shown that for inert gases a form of $\epsilon(r)$ in which $t=6$, $s=12$ gives good agreement with experiment. Values of U_0' for the $\{111\}$, $\{100\}$ and $\{110\}$ faces of the inert-gas crystals have been calculated from their heat of sublimation, using $K(6, 12)$, and are given in Table 3. They are compared with the value of the surface energies of the liquids extrapolated to 0° K. (Guggenheim 1945).

Table 3. Surface Energies of Inert-gas Crystals

	ϵ_0 (erg/atom)	a_0* (A)	${}_{111}U'_0$ (erg/cm²)	${}_{100}U'_0$ (erg/cm²)	${}_{110}U'_0$ (erg/cm²)	$U_{0\,\text{liq.}}$ (erg/cm²)
Ne	$4{\cdot}08 \times 10^{-14}$	2·26	17·2	17·9	18·7	15·1
A	13·89	2·70	41·1	42·7	44·7	36·3
Kr	19·23	2·79	53·3	55·3	57·9	
Xe	26·87	3·09	60·7	63·0	66·0	

* The lattice constant is λa_0.

The heats of sublimation at 0° K. were calculated by numerical integration from the latent heats at the boiling point, the heats of fusion and the specific heats of the solids and liquids; a correction $9\boldsymbol{k}\Theta/8$ for the zero point vibrations was made, Θ being the Debye temperature. No correction was made for the departure of the gases at atmospheric pressure from the perfect gas law. The experimental data are those of Clusius and his collaborators (1929, 1936, 1937, 1938, 1939).

The surface energies calculated for the crystal are greater than those found by experiment for the liquid. For inert gas crystals dU'_0/da is negative, but the difference in density of liquid and solid is not quite sufficient to account for the discrepancy.

The effect of zero-point vibrations on the surface energy has been neglected; for while they would invalidate any calculation for helium their effect on the surface energies of crystals formed from the heavier atoms will be small. In (ii) below it is shown that the decrease of energy U''_0 due to surface distortion is less than the uncertainties in the calculation of U'_0.

(ii) *Contribution of Surface Distortion to Surface Energy*

In inert-gas crystals the separation of the atomic planes parallel to the surface is greater near the surface than in the interior of the crystal. The surface energy of the distorted crystal is less than that of the unstable undistorted crystal by U''_0.

The distortion arises because of the interaction of atoms in non-adjacent planes. In the interior of a crystal (see Figure) the net force between all the atoms above the atomic plane $l=1$ on all the atoms below the plane is attractive. This is because, in homopolar crystals, the attractive forces decrease more slowly with distance than do the repulsive forces, and the separation of the parts of the crystal above and below $l=1$ is greater than the equilibrium distance. This attractive force is balanced by net repulsive forces between the atoms in the plane $l=1$ and the two parts of the crystal above and below $l=1$. If the part below $l=1$ is removed, so that $l=1$ becomes a surface plane, there is an unbalanced repulsive force which causes the atoms in the plane $l=1$ to move away from the rest of the crystal until the attractive and repulsive forces again become equal. Similar distortions occur for atoms in successive planes but these are very much smaller and will be neglected. The distortion will be least on crystal faces formed from close-packed planes, for these planes are most widely spaced and the forces between non-adjacent planes smallest. If it is possible to neglect the interaction between atoms that are not nearest neighbours the surface distortion is zero.

U_0'' is the decrease of potential energy when the surface plane of atoms moves from the position it occupied when at the centre of the crystal to its equilibrium position of minimum energy. Calculations of distortion and of U_0'' were made for the $\{100\}$ face of an inert-gas crystal ($s=12$, $t=6$). Distortion occurs by an equal displacement, in a direction perpendicular to the surface, of each atom in the plane $l=1$. The potential energy per atom of the surface plane with respect to the remainder of the crystal is:

$$\phi = C_{12}''\lambda a_0^{-12} - C_6''\mu a_0^{-6} \qquad \ldots\ldots(14)$$

where

$$C_s''(c) = \sum_{l\geqslant 2} (a_0/r)^s, \qquad \ldots\ldots(15)$$

and ca_0 is the distance of the surface plane, $l=1$, from the next plane, $l=2$. In equation (15) r is the distance between a particular atom in the surface plane and any atom in the remainder of the crystal; summation is over all atoms in the remainder of the crystal. In Table 9 values of C_6'' and C_{12}'' for a number of values of c are given. The equilibrium position of the surface plane occurs at the value of c for which ϕ is a minimum, viz.

$$dC_{12}''/dc = (2A_{12}''/A_6'')(dC_6''/dc). \qquad \ldots\ldots(16)$$

λa_0^{-12} and μa_0^{-6} have been eliminated by equation (11). A solution to equation (16) was found by numerical differentiation: $c_{\text{equil.}} = 1{\cdot}0254$. Thus in an inert-gas crystal the distance between the surface atomic plane and the next is, for a $\{100\}$ face, 2·5% greater than the distance in the interior of the crystal.

Values of the lattice sums at the equilibrium separation $c_{\text{equil.}}$ were obtained by interpolation and are included in Table 9. Then

$${}_{100}u_0'' = \Delta\phi = \Delta C_{12}''\lambda a_0^{-12} - \Delta C_6''\mu a_0^{-6}, \qquad \ldots\ldots(17)$$

where u_0'' is the decrease of ϕ as c increases from 1 to 1·0254, and $\Delta C_{12}''$ and $\Delta C_6''$ are the corresponding decreases in the lattice sums. As in the derivation of equation (12)

$${}_{100}u_0'' = 2(\Delta C_{12}''/A_{12}'' - 2\Delta C_6''/A_6'')\epsilon_0, \qquad \ldots\ldots(18)$$

$${}_{100}U_0'' = 0{\cdot}002\epsilon_0/a_0^2, \qquad \ldots\ldots(19)$$

${}_{100}U_0''$ is less than 1% of ${}_{100}U_0'$ and can be neglected because it is smaller than the inevitable errors in the calculation. Surface distortion will reduce the energy of a $\{111\}$ face in a somewhat less, and of a $\{110\}$ face in a somewhat greater proportion, but not sufficiently to affect appreciably the relative magnitudes of different faces.

§ 4. THE SURFACE ENERGIES OF IONIC CRYSTALS

(i) *Calculation of U_0'*

In crystals of the alkali-halides the alkali and halide ions are arranged on alternate points of a simple-cubic lattice. The halide ions have a negative charge of one electron and the alkali ions an equal positive charge. There are also van der Waals attractive forces and short range repulsive forces between the ions. Mayer and his colleagues (Born and Mayer 1932, Mayer and Helmholz 1932, Mayer 1933, Huggins and Mayer 1933) have considered these forces in detail and given numerical values for the force constants. According to them the potential between two alkali ions at a distance r apart can be written

$$\epsilon_{++}(r) = \mathbf{e}^2 r^{-1} - c_{++}r^{-6} - d_{++}r^{-8} + 1{\cdot}25 b_+^2 \exp(-r/\rho), \qquad \ldots\ldots(20)$$

the potential between two halide ions

$$\epsilon_{--}(r) = \mathbf{e}^2 r^{-1} - c_{--} r^{-6} - d_{--} r^{-8} + 0{\cdot}75 b_-^2 \exp(-r/\rho), \qquad \ldots\ldots(21)$$

and the potential between an alkali and halide ion

$$\epsilon_{+-}(r) = -\mathbf{e}^2 r^{-1} - c_{+-} r^{-6} - d_{+-} r^{-8} + b_+ b_- \exp(-r/\rho). \qquad \ldots\ldots(22)$$

The van der Waals terms proportional to the inverse sixth and inverse eighth power of the distance are referred to as the dipole–dipole and dipole–quadrupole interactions respectively; the latter term is small compared to the first. The repulsive potentials decrease exponentially with distance; in a crystal it is necessary to consider only the repulsion between an ion and its six nearest neighbours, which have opposite charge, and twelve next-nearest neighbours, which have the same charge.

If an ion is selected as origin all ions with the same charge have coordinates for which $m_1 + m_2 + m_3$ is even, ions with opposite charge have coordinates for which $m_1 + m_2 + m_3$ is odd. All planes (except $\{111\}$ planes) contain equal numbers of alkali and halide ions. To find the mutual potential between two parts of an alkali-halide crystal it is necessary to consider the potentials between (*a*) the alkali ions of part I and the alkali ions of part II, (*b*) the halide ions of part I and the halide ions of part II, (*c*) the alkali ions of part I and the halide ions of part II, (*d*) the halide ions of part I and the alkali ions of part II. The positions of the alkali and halide ions in the lattice are equivalent so that (*c*) and (*d*) are equal. The electrostatic contributions if considered separately diverge, and they must be grouped in pairs (*a*) and (*c*), (*b*) and (*d*), to obtain convergence; these two pairs are equal. As in equation (7) the mutual potential per alkali (or halide) ion in the surface plane is

$$\begin{aligned} -2u_0' = {} & -2B_e''' \mathbf{e}^2 a_0^{-1} - B_6''(c_{++} + c_{--}) a_0^{-6} - 2B_6' c_{+-} a_0^{-6} \\ & - B_8''(d_{++} + d_{--}) a_0^{-8} - 2B_8' d_{+-} a_0^{-8} \\ & + N''(1{\cdot}25 b_+^2 + 0{\cdot}75 b_-^2) \exp(-\sqrt{2} a_0/\rho) \\ & + 2N' b_+ b_- \exp(-a_0/\rho), \end{aligned} \qquad \ldots\ldots(23)$$

where a_0 is the alkali-halide ion distance, B_e''' is an electrostatic lattice sum

$$B_e''' = \sum_{\substack{l \geq 1 \\ m_1+m_2+m_3 \text{ odd and even}}} \frac{l(-1)^{m_1+m_2+m_3}}{(m_1^2 + m_2^2 + m_3^2)^{\frac{1}{2}}}, \qquad \ldots\ldots(24)$$

the factor $(-1)^{m_1+m_2+m_3}$ arising because of the opposite sign of ions at alternate lattice points; the B_l's represent the lattice sums for the van der Waals interaction between alkali and halide ions:

$$B_l' = \sum_{\substack{l \geq 0 \\ m_1+m_2+m_3 \text{ odd}}} \frac{l}{(m_1^2 + m_2^2 + m_3^2)^{l/2}}; \qquad \ldots\ldots(25)$$

N' and N'' are respectively the number of nearest and next-nearest bonds per surface ion that cross the plane of section. Values of the lattice sums (divided by $2\omega_p$) for $\{100\}$ and $\{110\}$ faces are given in Table 4, and their method of calculation is described in § 5.

The surface energy per unit area, U_0', is $u_0'/\omega_p a_0^2$, where $1/\omega_p a_0^2$ is the number of alkali (or halide) ions per unit area in the surface plane. The force constants given by Huggins and Mayer (1933) for sodium and potassium halides were used to calculate the contributions to U_0' of the electrostatic, dipole–dipole, dipole–quadrupole and repulsive forces. These contributions and their total are given in Table 5 for a {100} face.

In Table 6 are given the surface energies ${}_{110}U_0'$ of a {110} face, the ratio ${}_{110}U_0'/{}_{100}U_0'$ and a_0. For consistency a_0 was calculated from the force constants.

The electrostatic term is predominant in the lattice energy, and the repulsive and van der Waals terms are only one-tenth and one-thirtieth of the electrostatic term. This is not so for the surface energy : here the electrostatic term (positive) is only a little greater than the repulsive term (negative), so that van der Waals forces give rise to almost half of the net surface energy. This is because U_0' is the energy necessary to divide a crystal into two neutral parts, whilst the lattice energy is the energy necessary to divide it into oppositely charged ions. The large ratio of the surface energy of a {110} to a {100} face arises mainly from the difference between the electrostatic terms; this is clear from Table 4.

Table 4. Lattice Sums used to Calculate the Surface Energies of Alkali-halides

	$B_e'''/2\omega_P$	$B_6''/2\omega_P$	$B_6'/2\omega_P$	$B_8''/2\omega_P$	$B_8'/2\omega_P$	$N''/2\omega_P$	$N'/2\omega_P$
{100}	0·01631	0·17670	0·33820	0·06920	0·26898	1·00000	0·25000
{110}	0·03174	0·18618	0·43482	0·07353	0·36972	1·06066	0·35355

Table 5. The Contributions of the Different Forces to U_0' for {100} Faces (erg/cm²)

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI
Electrostatic	618·0	345·6	289·7	227·8	396·5	250·3	215·8	175·8
Dipole–dipole	82·8	79·6	77·9	76·2	84·1	69·8	65·0	60·6
Dipole–quadrupole	8·8	8·6	8·4	8·4	8·3	7·2	6·6	6·3
Repulsive	−500·3	−245·3	−199·3	−151·9	−294·3	−164·3	−136·2	−106·4
Total	209	189	177	161	195	163	151	136

Table 6. The Surface Energy, U_0', of a {110} Face

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI
${}_{110}U_0'$ (erg/cm²)	640·5	445·3	396·2	337·9	483·1	352·3	316·7	273·6
${}_{110}U_0'/{}_{100}U_0'$	3·06	2·36	2·24	2·11	2·48	2·16	2·09	2·01
a_0 (A.)	2·290	2·780	2·948	3·194	2·655	3·095	3·252	3·482

In the alkali-halide crystals the {111} planes are formed alternately from alkali and halide ions, and there appears no simple method of evaluating the electrostatic contribution to the surface energy of a {111} face.

(ii) *Contribution of Surface Distortion to Surface Energy*

Lennard-Jones and Dent (1928 a) and Dent (1929) showed that in ionic crystals the most important cause of surface distortion and corresponding decrease of surface energy U_0'' is the polarization of the surface ions in the electrostatic field.

Verwey (1946) has made detailed calculations and shows that, in general, the positive ions at the surface are displaced away from the crystal and the negative surface ions displaced towards the crystal. He shows that for NaBr U_0'' is 32 erg/cm². It is supposed that NaBr is typical, and ${}_{100}U_0$ for the other crystals obtained by reducing ${}_{100}U_0'$ in the same proportion. In Table 7 values of ${}_{100}U_0'$ are compared with the experimental values of the liquid, which have been extrapolated to 0° K. by Jaeger (1917).

Table 7. Surface Energies ${}_{100}U_0$ of the {100} Face (erg/cm²)

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI
${}_{100}U_0$	171	155	145	132	160	134	124	111
$U_{0(\text{liq.})}$	335	190	178	138	242	173	159	139

Although for alkali-halide crystals dU_0'/da is positive, the decrease of density on fusion is not sufficient to account for the discrepancy between the two values.

§ 5. THE EVALUATION OF LATTICE SUMS

(i) *Computation of B_t'' and B_t'*

In order to evaluate lattice sums of the form

$$B_t'' = \sum_{\substack{l\geqslant 1 \\ m_1+m_2+m_3 \text{ even}}} \frac{l}{(m_1^2+m_2^2+m_3^2)^{t/2}}, \qquad \ldots\ldots(26)$$

it is necessary to express l, the ordinal of the plane in which an atom lies, in terms of the coordinates of the atom. The relation is different for different planes

$$l_{111}=(m_1+m_2+m_3)/2, \quad l_{100}=m_1, \quad l_{110}=m_1+m_2, \qquad \ldots\ldots(27)$$

where m_1, m_2, m_3 are integers (positive, negative or zero). The values of l for any value of $(r/a_0)^2=m_1^2+m_2^2+m_3^2$ are readily enumerated, and the contributions to B_t'' of all atoms (of part I of the crystal) that are within or on a hemisphere centre O and radius r_1 can be found by direct summation. When t is greater than 10 the sum converges rapidly and an accurate value of B_t'' can be obtained if the contributions of atoms outside a hemisphere radius $\sqrt{30}a_0$ be neglected. For smaller values of t the contributions even of those atoms that are outside a hemisphere radius $\sqrt{50}a_0$ cannot be neglected, and they must be estimated by integration.

Before finding the contributions to B_t'' of those atoms outside a hemisphere radius r_1, a more general expression that gives the contributions of these atoms to the mutual potential, $-2U_0'$, in terms of $\epsilon(r)$ will be derived. For distant atoms each atomic plane can be regarded as a uniform lamella which extends a distance $h/2$ above and below the plane; their contribution to $-2U_0'$ is, by equation (4),

$$I=\frac{n}{h}\iiint z\epsilon(r)\,dV, \qquad \ldots\ldots(28)$$

n is the number of atoms per unit volume, the element of volume dV is at a distance r from O, and z from the plane $l=0$ (see Figure). The continuum representing part I of the crystal extends to the plane $l=\frac{1}{2}$; so the region of integration is that portion of the semi-infinite volume bounded by the plane $l=\frac{1}{2}$ that is outside the hemisphere radius r_1'. This region is the difference of two other regions: (*a*) the semi-infinite volume above the plane $l=0$ and outside the hemisphere r_1', (*b*) the portion of the infinite slab lying between the planes $l=0$ and $l=\frac{1}{2}$ that is outside the cylinder radius r_1'. The integrals over the two regions are written in spherical and cylindrical coordinates respectively, and in the second integral the approximation is made of putting the cylindrical radial coordinate equal to r, the distance of a volume element from O.

$$I=\frac{n}{h}\int_{r_1'}^{\infty}\int_{0}^{\pi/2}\int_{0}^{2\pi} r^3\epsilon(r)\cos\theta\sin\theta\,d\phi\,d\theta\,dr-\frac{n}{h}\int_{r_1'}^{\infty}\int_{0}^{h/2}\int_{0}^{2\pi} r\epsilon(r)z\,d\phi\,dz\,dr. \quad \ldots\ldots(29)$$

$$I=\pi\frac{n}{h}\int_{r_1'}^{\infty} r^3\epsilon(r)\,dr-\frac{\pi}{4}nh\int_{r_1'}^{\infty} r\epsilon(r)\,dr. \quad \ldots\ldots(30)$$

In a face-centred-cubic lattice

$$n=1/2a_0^3 \qquad \text{and} \qquad nh=1/\omega_{\mathrm{P}}a_0^2, \quad \ldots\ldots(31)$$

so if $\epsilon(r)$ contains a term λr^{-t} the contribution of the integrals to B_t'' is

$$\frac{\pi\omega_{\mathrm{P}}}{4(t-4)(r_1'/a_0)^{t-4}}-\frac{\pi}{4\omega_{\mathrm{P}}(t-2)(r_1'/a_0)^{t-2}}.$$

In order that the contributions to B_t'' of atoms on the surface of the hemisphere r_1 should not be included in both the sum and the integral, the lower limit of integration r_1' was defined by

$$r_1'/a_0=(3/2\pi)^{\frac{1}{3}}N^{\frac{1}{3}}, \quad \ldots\ldots(32)$$

where N is the number of atoms that are in and on a sphere centre O and radius r_1, and $4\pi r_1'^3/3$ is the volume of continuum these N atoms would occupy. To compute B_6'' it was necessary to find by direct summation the contributions of all atoms within a hemisphere radius $\sqrt{50}a_0$. B_t'' is tabulated in Table 8 for {111}, {100}, and {110} faces for t between 6 and 12.

Table 8. The Lattice Sum B_t''

t	6	7	8	9	10	11	12
${}_{111}B_t''$	0·56593	0·33264	0·21428	0·14391	0·09873	0·068545	0·047914
${}_{100}B_t''$	0·70680	0·42387	0·27680	0·18765	0·12960	0·090387	0·063389
${}_{110}B_t''$	1·0532	0·63547	0·41596	0·28218	0·19486	0·135863	0·095244

Similar computations were made for B_t' and the results, in the form $B_t'/2\omega_{\mathrm{P}}$, are given in Table 4.

(ii) *Computation of* C_6'' and C_{12}''

In the computation of C_6'' the contributions of all atoms inside and on a cylinder whose radius was $\sqrt{50}a_0$, and whose bases were on the planes $l=2$–7, were found by direct summation. The contributions of those atoms in the planes $l=2$–7 that are outside this cylinder were found by integrating separately for each plane; a lower limit of integration given by an equation analogous to (32) was used. The contributions of atoms in the planes $l>7$ were found by a single integration; the lower limit of integration was taken as $l=7{\cdot}5$. C''_{12} converged so rapidly that it was sufficient merely to sum atoms inside and on a cylinder radius $\sqrt{14}a_0$ that lay between the planes $l=2$ and $l=4$. C''_6 and C''_{12} are given in Table 9 for values of c between 1·00 and 1·04.

Table 9. The Lattice Sums C''_6 and C''_{12} *

c	1·00	1·01	1·02	1·03	1·04	1·0254
C''_6	0·612195	0·595823	0·579923	0·564479	0·549472	0·571527
C''_{12}	0·063028	0·059367	0·055920	0·052673	0·049616	0·054144

* Individual values are not accurate to this number of figures but the set is consistent.

(iii) *Computation of* B_e'''

Previous calculations of B_e''' for {100} and {110} faces of sodium-chloride type crystals have been made by Born and Stern (1919). The atomic planes parallel to these faces are neutral and their potentials decrease very rapidly in a normal direction. Using Madelung's method (see for example Lennard-Jones and Dent 1928 b), Born and Stern evaluated the potentials of the planes $l=1, 2, 3$, and found they could neglect the others. Their value of ${}_{110}B_e'''$ is used in this paper.

It is possible rapidly to evaluate ${}_{100}B_e'''$ for a {100} plane by an elementary method of direct summation similar to one suggested by Slater (1939) for the evaluation of Madelung's constant. If the contributions of positive and negative ions to B_e''' are summed separately, both diverge; convergence is possible only if the net charge on all the ions included in the sum is zero. If rapid convergence is to occur the domain of summation must be such that all ions outside it can be grouped so that every group has zero charge and makes only a small contribution to the potential at O (see Figure).

First, an approximate value of the potential at O due to each of the planes $l=1$—5 was found by summing over all the ions of a plane inside and on a square with centre on the normal cube axis through O and sides parallel to the other cube axes. In order that such a square be neutral an ion on a side was treated as only half in the square and an ion at the corner as only a quarter in the square. The potentials of each plane $l_1\mathbf{e}/a_0$, $l_2\mathbf{e}/a_0$, $l_3\mathbf{e}/a_0$ etc. thus calculated, converged somewhat slowly as the size of the square was increased. The errors, which arise because of ions not included in the sum, have opposite signs for adjacent planes, since in adjacent planes positive and negative ions interchange their positions. If the planes are grouped in threes and the middle plane given double weight, the potential of the triplet rapidly converges; this is because the error of the centre sum is almost the mean of the errors of the exterior sums and has opposite sign.

The two triplets, $l_1+2l_2+l_3$ and $2(l_3+2l_4+l_5)$, were evaluated using a square of side $10a_0$; this gave a value of B_e''' $(=l_1+2l_2+3l_3\ldots.)$ equal to 0·06525. The second triplet was only 1% of the first.

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On the Surface Free Energy of Certain Metals

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ABSTRACT. For the purpose of calculating the surface energy and surface double layer for a number of monovalent metals, a simple and yet adequate model is proposed, which does not have the disadvantages of models employed by previous authors. In this the valence electrons are treated according to a simple Sommerfeld model, and the positive charge of the ions is distributed uniformly through the metal. It is shown that by a suitable combination of the methods of Thomas–Fermi and of direct wave mechanics, both the surface energy and the strength of the double layer can be calculated. The surface double layers for the metals considered are found to lie in the range 0·1–0·5 ev. The contribution to the surface energy from the electrostatic energy in the double layer is found to be very small. In estimating the surface energy, the electrons in a metal can be considered as moving in a box with finite potential walls of suitably determined height ϕ. A temperature-dependent term in the surface free energy due to the change in lattice vibrations caused by the free surface is also considered. The surface energies obtained from ϕ determined in two independent ways agree closely and are found to agree with the experimental values of the surface tension of the liquid metals to within a factor 1·5.

§ 1. INTRODUCTION

In spite of the high values of the surface tension exhibited by metals, it is an interesting fact that the ratio of the surface energy per surface atom to the heat of vaporization per atom is for monovalent metals of the order of 1 : 7, for zinc and cadmium about 1 : 3·5 and for mercury about 1 : 2·4, whereas for many other substances the ratio is of the order 1 : 2.

Shuttleworth (1949) has discussed the values of this ratio arising from various simple laws of force, applicable in ionic and molecular crystals, and finds results varying from 1 : 2 to 1 : 4 according to the law of force.

In the present work we show that the peculiarly low values of surface tension in monovalent metals result directly from the properties of the free electron gas. The model used is certainly fairly adequate for the monovalent metals in the solid state, so the surface free energy of the solid at the melting point has been calculated for these substances for comparison with the measured surface tension of the liquid. The calculated values are about 1·5 times the observed.

§ 2. REVIEW OF EARLIER WORK

The surface energy of metals has been treated theoretically by several workers (Frenkel 1917, Gogate and Kothari 1935, Dorfman 1943, Samoilovich 1945, Brager and Schuchowitzky 1946a, b). However, only the last two investigations are relevant to the present article. We shall consider briefly the models and methods employed by these authors before discussing those of the present work.

Samoilovich replaced the lattice of ions by a uniform distribution of positive charge and employed the Thomas–Fermi statistical method, according to which the total energy of the electrons is completely determined by the electron density distribution. The positive surface energy thus obtained, however, arises entirely from the use of the Weizsäcker term, which corrects for the kinetic energy associated with the rapid change of electron density at the metal surface. This may easily be seen, since the original Thomas–Fermi method would give zero surface energy for that distribution of electron charge (not a solution of the Thomas–Fermi equation) which is uniform over the region containing the positive cloud and zero elsewhere. The distribution which satisfies the Thomas–Fermi equation, having lower energy (Lenz 1932), then gives a negative value for the surface energy.

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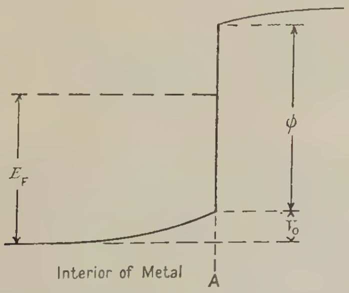
Apart from the uncertainty of the Weizsäcker correction, this model makes no allowance for the different ionic fields of different metals, the surface tension being determined entirely by the density of positive charge which depends only on the valency and density of the metal.

In view of Samoilovich's result, that the positive surface energy is due to the increase in kinetic energy of the electrons imposed by the steep potential barrier at the surface, Brager and Schuchowitzky treated this effect by the direct wave-mechanical consideration of free electrons enclosed in a box with impenetrable walls, at which the wave function vanishes. They found that the total energy contained a term proportional to the surface and identified this term as the surface energy. This model neglects the electrical double layer at the surface and, more important, the finite values of the work function of real metals.

§ 3. THE MODEL

It is possible to find for the monovalent metals Li, Na, K, Rb, Cs, Cu, Ag, Au a model which avoids the faults of the two so far considered. Theoretical work on binding energy has shown that in these metals the positions of the conduction electrons are so strongly correlated that we may regard each electron as moving at any instant only in the field of the ion nearest to it, other ions being neutralized by the electrons on them. Then to a good approximation the electrons behave as free electrons at a constant potential V, where $-\boldsymbol{e}V$ is the mean potential energy between an electron and its nearest ion. The potential naturally vanishes outside a metal surface so that we have essentially a Sommerfeld picture of the metal. Thus the model we adopt is as follows. The positive charge of the metal ions is supposed to be uniformly distributed over a volume proportional to the number of ions. At the boundary of this volume we imagine a finite discontinuous jump in potential. The variation in potential energy of an electron as it passes through the surface is then as shown in the Figure.



The approximately exponential rise in the potential energy outside the boundary arises from the overlap of the wave functions beyond A. There is thus a distribution of negative charge in this region which may be calculated by wave mechanics from the electron distribution inside the boundary. The latter is calculated by the Thomas–Fermi statistical method. The conditions that an equal resultant positive charge must remain inside the metal and that the field must vanish in the interior of the metal determine the solution uniquely.

The electronic surface energy is then divided into two terms : (i) that which results from "compressing" the electron gas within the potential well; this gives a smaller term than one would obtain if ϕ were taken to be infinite as in the Russian work; (ii) the electrostatic energy of the double layer : this is found to be small.

(i) *Charge Penetration*

We first find the relation between the charge density outside and inside the surface. If we take the x-axis normal to the surface ($x=0$), the wave function representing a stream of electrons with momentum P incident on the surface at an angle θ from the normal and undergoing reflection is

$$\begin{aligned}\psi_1 &= A(2\boldsymbol{m}\phi)^{\frac{1}{2}} \exp\left[iP(y\sin\theta + x\cos\theta + \alpha)/\hbar\right] \\ &\quad + A(2\boldsymbol{m}\phi)^{\frac{1}{2}} \exp\left[iP(y\sin\theta - x\cos\theta - \alpha)/\hbar\right], \qquad x<0 \qquad \ldots\ldots(1) \\ \psi_2 &= 2AP\cos\theta\exp\left[(iPy\sin\theta - \beta x)/\hbar\right], \qquad x>0\end{aligned}$$

where $\tan(\alpha P/\hbar) = \beta/P\cos\theta$ and $\beta = \sqrt{(2\boldsymbol{m}\phi - P^2\cos^2\theta)}$. The density $\rho(P,\theta)$ of electrons in the incident beam is

$$\rho(P,\theta) = |A|^2 2\boldsymbol{m}\phi. \qquad \ldots\ldots(2)$$

The number of particles per unit area outside the surface is then

$$\int_0^\infty |\psi_2|^2\,dx = \hbar\rho(P,\theta)P^2\cos^2\theta/\boldsymbol{m}\phi\beta. \qquad \ldots\ldots(3)$$

In the Thomas–Fermi method the particle velocities at any point are random in direction; thus the density of electrons incident on the surface in the range of inclination to the normal from θ to $\theta+d\theta$ and for momentum from P to $P+dP$ is given by

$$\rho(P,\theta)\,dP\,d\theta = 4\pi\boldsymbol{h}^{-3}P^2\sin\theta\,dP\,d\theta.$$

Thus for the whole Fermi distribution the number n_2 of electrons outside the surface per unit area is given by substituting for $\rho(P,\theta)$ in (3) and integrating over P and θ; the result is

$$\begin{aligned}n_2 &= \frac{2}{\boldsymbol{m}\phi\boldsymbol{h}^2}\int_0^{P_{\mathrm{m}}} dP\int_0^{\frac{1}{2}\pi}\frac{P^4\cos^2\theta\sin\theta}{\sqrt{(2\boldsymbol{m}\phi - P^2\cos^2\theta)}}\,d\theta \\ &= \frac{2\boldsymbol{m}\phi}{\boldsymbol{h}^2}\left\{\left(\frac{3}{4} - \frac{P_{\mathrm{m}}^2}{4\boldsymbol{m}\phi}\right)\sqrt{\left[\frac{P_{\mathrm{m}}^2}{2\boldsymbol{m}\phi}\left(1 - \frac{P_{\mathrm{m}}^2}{2\boldsymbol{m}\phi}\right)\right]} - \left(\frac{3}{4} - \frac{P_{\mathrm{m}}^2}{2\boldsymbol{m}\phi}\right)\sin^{-1}\sqrt{\left(\frac{P_{\mathrm{m}}^2}{2\boldsymbol{m}\phi}\right)}\right\}. \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \ldots\ldots(4)\end{aligned}$$

Here P_{m} is the maximum momentum in the Thomas–Fermi distribution just inside the surface and the dimensionless quantity $P_{\mathrm{m}}^2/2\boldsymbol{m}\phi$ is the ratio of the corresponding maximum kinetic energy of the electrons to the potential energy discontinuity ϕ.

(ii) *The Thomas–Fermi Equation*

Let E_{m} be the maximum electronic energy and V at any point the electrostatic potential measured from that in the interior of the metal; then having regard to the constant density of positive charge inside the surface the Thomas–Fermi equation may be set up in the usual way :

$$\frac{d^2V}{dx^2} = -4\pi\left\{-\boldsymbol{e}\frac{8\pi}{3\boldsymbol{h}^3}[2\boldsymbol{m}(E_{\mathrm{m}}+\boldsymbol{e}V)]^{3/2}+\frac{3\boldsymbol{e}}{4\pi r_0^3}\right\} \qquad \ldots\ldots(5)$$

where $4\pi r_0^3/3 = v_0$ is the atomic volume. When the dimensionless quantities

$$g=(E_{\mathrm{m}}+\boldsymbol{e}V)/E_{\mathrm{F}}, \qquad \xi = x/(r_0^3E_{\mathrm{F}}/3\boldsymbol{e}^2)^{\frac{1}{2}} \qquad \ldots\ldots(6)$$

where $E_{\mathrm{F}}=(9\pi/4)^{2/3}\hbar^2/2\boldsymbol{m}r_0^2$ are introduced, (5) becomes

$$d^2g/d\xi^2 = g^{3/2}-1. \qquad \ldots\ldots(7)$$

We notice that $V \to 0$ in the interior of the metal, where $E_{\mathrm{m}} = E_{\mathrm{F}}$, so that $g=1$ corresponds to the distribution of one electron per atom, as in the interior far from the surface. We shall find the deviation of g from 1 to be small in the cases to be treated. It is thus for our purpose more convenient and sufficiently accurate to solve (7) approximately to the second order by setting

$$g = 1-\Delta \qquad \ldots\ldots(8)$$

and treating Δ as small compared with unity.

On substituting (8) in (7) and expanding $g^{3/2}$, we find

$$d^2\Delta/d\xi^2 = 3\Delta/2 - 3\Delta^2/8 \qquad \ldots\ldots(9)$$

when terms of degree higher than the second are neglected.

The asymptotic solution for large negative ξ (interior of metal) must clearly be of the form

$$\Delta \sim A\exp[\xi\sqrt{(3/2)}] \quad \text{as} \quad \xi \to -\infty. \qquad \ldots\ldots(10)$$

Thus A is the only arbitrary constant to be determined. The approximate solution of (9), to the same order of accuracy as (9), which has the asymptotic form (10) is

$$\Delta = A\exp[\xi\sqrt{(3/2)}] - [A^2\exp(\xi\sqrt{6})]/12$$

or

$$g = 1 - A\exp[\xi\sqrt{(3/2)}] + [A^2\exp(\xi\sqrt{6})]/12. \qquad \ldots\ldots(11)$$

If the electrostatic field is to vanish at large distances, the sum of the resultant charges inside and outside the surface must vanish. This condition determines A.

The electron density is proportional to $g^{3/2}$. Since when $g=1$ the density of electrons is $3/4\pi r_0^3$, the net charge density for any value of g is

$$\sigma_1\boldsymbol{e} = \frac{3\boldsymbol{e}}{4\pi r_0^3}(1-g^{3/2}) \qquad \ldots\ldots(12)$$

and the total charge $n_1\boldsymbol{e}$ per unit area inside the surface is thus given by

$$n_1\boldsymbol{e} = \frac{3\boldsymbol{e}}{4\pi r_0^3}\int_{-\infty}^{0}(1-g^{3/2})\,dx. \qquad \ldots\ldots(13)$$

Using (7) and (10), we find on integrating

$$n_1\boldsymbol{e} = -\frac{3\boldsymbol{e}}{4\pi r_0^2}\left(\frac{r_0E_{\mathrm{F}}}{3\boldsymbol{e}^2}\right)^{\frac{1}{2}}g_0' \qquad \ldots\ldots(14)$$

where $g_0 = (dg/d\xi)_{\xi=0}$.

We have now to eliminate P_{m} from the expression (4) for the charge outside the surface. Just inside, we have $P_{\mathrm{m}}^2/2\boldsymbol{m} = E_{\mathrm{m}} + \boldsymbol{e}V = E_{\mathrm{F}}g_0$ where $g_0 = (g)_{\xi=0}$, so that n_2 can be expressed as a function of g_0 :

$$n_2 = \frac{2\boldsymbol{m}\phi}{\boldsymbol{h}^2}\left\{\left(\frac{3}{4}-\frac{g_0}{2\lambda}\right)\sqrt{\left[\frac{1}{\lambda}\left(1-\frac{g_0}{\lambda}\right)\right]} - \left(\frac{3}{4}-\frac{g_0}{\lambda}\right)\sin^{-1}\sqrt{\left(\frac{g_0}{\lambda}\right)}\right\} \qquad \ldots\ldots(15)$$

where $1/\lambda = E_{\mathrm{F}}/\phi$. It is possible to express g_0', g_0 in terms of A

$$g_0 = 1 - A + A^2/12; \qquad g_0' = -[A - A^2/6]\sqrt{(3/2)} \qquad \ldots\ldots(16)$$

and A is then determined by the numerical equality of the charges inside and outside the surface,

$$n_1(A) = -n_2(A). \qquad \ldots\ldots(17)$$

Thus knowing r_0 and ϕ we can calculate the charge distribution near the surface. In the cases to be discussed we find that (17) can easily be solved by successive approximations, taking as the first, $g_0 = 1$ in (15).

§4. THE ELECTRICAL DOUBLE LAYER

The strength of the surface double layer is measured by the total change in electrostatic potential energy of an electron taken through the double layer; it is thus given by

$$-\boldsymbol{e}[V(\infty) - V(-\infty)] = -\boldsymbol{e}V(\infty), \qquad \ldots\ldots(18)$$

since we have taken the potential energy to be zero in the interior of the metal.

To evaluate $V(\infty)$, the charge distribution outside the surface may be approximated by an exponential function

$$\sigma_2(x) = C\exp(-qx). \qquad \ldots\ldots(19)$$

The density at $x = 0$ is C, which should be equal to the density obtained by integrating the wave mechanical solution $|\psi_2(0)|^2$ as given by (1). Thus we find

$$C = \frac{16\pi}{15}\left(\frac{P_{\mathrm{m}}}{\boldsymbol{h}}\right)^3 \frac{P_{\mathrm{m}}^2}{2\boldsymbol{m}\phi} \qquad \ldots\ldots(20)$$

q is then determined from the total charge:

$$n_1 = |n_2| = \int_0^\infty \sigma_2(x)\,dx = C/q. \qquad \ldots\ldots(21)$$

The potential $V(x)$ for $x > 0$ can then be determined from the Poisson's equation

$$d^2V(x)/dx^2 = 4\pi\boldsymbol{e}\sigma_2(x) = 4\pi\boldsymbol{e}C\exp(-qx). \qquad \ldots\ldots(22)$$

At $x = 0$ the approximate solution must be equal to the potential just within the surface, given by

$$-\boldsymbol{e}V_0 + P_{\mathrm{m}}^2/2\boldsymbol{m} = E_{\mathrm{m}} = E_{\mathrm{F}} \quad \text{or} \quad \boldsymbol{e}V_0 = -E_{\mathrm{F}}(1 - g(0)). \qquad \ldots\ldots(23)$$

The solution satisfying this boundary condition and the condition that the field vanishes at infinity is

$$V = 4\pi\boldsymbol{e}C\{\exp(-qx) - 1\}/q^2 - E_{\mathrm{F}}(1 - g(0))/\boldsymbol{e}. \qquad \ldots\ldots(24)$$

So we find for the strength of the double layer

$$-\boldsymbol{e}V(\infty) = 4\pi\boldsymbol{e}^2C/q^2 + E_{\mathrm{F}}(1 - g(0)). \qquad \ldots\ldots(25)$$

We may put this into a more convenient form for calculation by substitution from (14), (21) and (22)

$$-\boldsymbol{e}V(\infty) = E_{\mathrm{F}}g_0[1 + 5g_0^{-5/2}g_0'^2/2\lambda] \qquad \ldots\ldots(26)$$

where g_0, g_0' are defined as above. Numerical values for the metals considered are given in Table 1.

§ 5. THE SURFACE ENERGY

The calculation of surface energy on this model must take account of three terms : The effect dealt with by Brager and Schuchowitzky (1946a, b) which assumes impenetrable boundaries, the penetration of the barrier, and the energy of formation of the electrical double layer. The first two terms arise directly from wave-mechanical considerations, and are not really physically separable, but it is mathematically convenient to treat them separately.

(i) *The Term of Brager and Schuchowitzky*

This term is due to the increase of kinetic energy consequent on the impenetrability of the walls. Mathematically this condition is expressed in the requirement that the standing electron waves should have nodes at the walls. If we consider a cubical box of length L, then in the wave function $\psi = \sin k_x x \sin k_y y \sin k_z z$ the wave numbers k_x, k_y, k_z must have respectively the values $l\pi/L$, $m\pi/L$, $n\pi/L$ where l, m, n are positive integers.

Table 1

Metal	Cu	Ag	Au	Li	Na	K	Rb	Cs
E_F (ev.)	7·05	5·5	5·5	4·7	3·15	2·03	1·77	1·52
ϕ (ev.)..	15·4	13·7	16·3	9·85	8·13	6·48	6·09	5·62
S_1+S_2 (erg cm^{-2})	2180	1400	1490	960	470	208	165	125
S_3 (erg cm^{-2}) ..	8·0	2·3	2·2	4·5	1·3	0·32	0·2	0·12
$-F_s$ (erg cm^{-2})..	360	257	240	66	34	25	21	18
σ (erg cm^{-2}) ..	1820	1140	1250	890	440	180	140	110
σ (exp.) (erg cm^{-2})	1100	800	600–1000	—	290	200–400	—	—
Double layer (ev.)	0·55	0·29	0·28	0·43	0·25	0·12	0·10	0·08

S_1+S_2	is the surface energy arising from the change in kinetic energy of the electron gas due to the presence of the surface.
F_s	is the surface free energy arising from the change in thermal vibrations.
S_3	is the electrostatic energy of the surface double layer.
σ	is the surface free energy obtained from these three terms.

These discrete states are conveniently represented as lattice points in the space (k_x, k_y, k_z) with lattice constant π/L. The number of occupied lattice points, multiplied by a factor 2 to allow for the alternative spin states, must be equal to the number of electrons to be accommodated and the total kinetic energy is the sum of

$$\hbar^2(k_x^2+k_y^2+k_z^2)/2m \qquad \ldots\ldots(27)$$

over the occupied states. An energy proportional to L^3 is obtained if we assume that the number of lattice points in a spherical octant of volume $\pi k_{\mathrm{m}}^3/6$ is just $L^3 k_{\mathrm{m}}^3/\pi^2$ and that the average energy is simply the integral average of (27) throughout the sphere. Clearly this procedure counts also points on the basal planes, but with weight $\frac{1}{2}$. These however do not represent permitted states since the corresponding wave functions vanish everywhere if they are zero on the walls.

These rejected points must be made good by taking just half as many at the surface of the sphere. The total energy corresponding to those points which were wrongly included is

$$3\left(\frac{L}{\pi}\right)^2 \frac{2\pi}{4} \int_0^{k_{\mathrm{m}}} \frac{\hbar^2 k^2}{2m}\, k\, dk = \frac{3\pi}{16m}\left(\frac{L\hbar}{\pi}\right)^2 k_{\mathrm{m}}^4. \qquad \ldots\ldots(28)$$

The total number of states thus rejected is $3(L/\pi)^2\pi k_{\rm m}^2/4$. The energy necessary to make them good at the surface of the sphere is

$$3\left(\frac{L}{\pi}\right)^2\frac{\pi k_{\rm m}^2}{4}\cdot\frac{\hbar^2k_{\rm m}^2}{2\boldsymbol{m}}. \qquad \ldots\ldots(29)$$

Thus the Brager–Schuchowitzky correction, which is the difference of (29) and (28), becomes $3\pi(L/\pi)^2\hbar^2k_{\rm m}^4/16\boldsymbol{m}$. Since the total surface of the cube is $6L^2$ this is equivalent to a surface energy

$$S_1=\pi P_{\rm m}^4/8\boldsymbol{h}^2\boldsymbol{m} \text{ per unit area.} \qquad \ldots\ldots(30)$$

Brager (1947) has further shown that the same expression is obtained for a spherical mass of material, so that its identification as a surface energy is reasonable.

(ii) *Term due to Barrier Penetration*

Since the potential energy step at the surface of the metal is actually finite, electrons penetrate the barrier and their wave functions are not zero at the boundary. In fact each wave function has a definite shift in phase as though it possessed a virtual node a little outside the boundary, and there is a corresponding decrease in the energy of that state. Let us consider a cube of edge L as in the above section; suppose it to lie entirely in the region $x<0$ and let the face $x=0$ alone have a finite potential barrier, the others remaining infinite. We see that in equations (1), only the factor dependent on x is affected by the barrier. If we write $\hbar^{-1}P\cos\theta=k_x$ this factor becomes

$$\alpha\sin(k_xx-\delta) \qquad \ldots\ldots(31)$$

where

$$\tan\delta=k_x/\sqrt{(2\boldsymbol{m}\phi/\hbar^2-k_x^2)}. \qquad \ldots\ldots(32)$$

Thus the wave function has a phase-shift δ at the boundary which tends to zero as ϕ increases.

The boundary condition at the opposite wall, i.e. at $x=-L$, requires that $\sin(-k_xL-\delta)=0$, whence

$$k_x=l\pi/L-\delta/L, \qquad \ldots\ldots(33)$$

where l is an integer. Thus the substitution of the finite for the infinite barrier reduces k_x for each state by δ/L, corresponding to an energy change

$$\Delta E=\hbar^2\Delta(k_x^2+k_y^2+k_z^2)/2\boldsymbol{m}=-(\hbar^2/\boldsymbol{m})k_x(\delta/L). \qquad \ldots\ldots(34)$$

The number of states with k_x in the range dk_x is

$$\tfrac{1}{2}\pi(k_{\rm m}^2-k_x^2)(L/\pi)^3\,dk_x. \qquad \ldots\ldots(35)$$

Thus when L is large the energy change per unit surface is given by the integral

$$S_2=\frac{\Sigma\Delta E}{L^2}=-\frac{\hbar^2}{2\pi^2\boldsymbol{m}}\int_0^{k_{\rm m}}(k_{\rm m}^2-k_x^2)k_x\tan^{-1}\left[\frac{k_x}{\sqrt{(2\boldsymbol{m}\phi/\hbar^2-k_x^2)}}\right]dx. \qquad \ldots\ldots(36)$$

The integral is easily evaluated to give

$$S_2=-\frac{P_{\rm m}^4}{16\boldsymbol{m}\boldsymbol{h}^2}\{3(2-\lambda)\sqrt{(\lambda-1)}+[3\lambda^2-8\lambda+8]\sin^{-1}\lambda^{-\frac{1}{2}}\} \qquad \ldots\ldots(37)$$

where, as before, $\lambda=\phi/E_{\rm F}$.

(iii) *The Energy of Formation of the Electrical Double Layer*

Apart from the changes in kinetic energy, the energy of electrostatic interaction within the system is increased by the formation of the double layer. By some authors the surface energy has been attributed entirely to this source. In fact, however, we shall see that the electrostatic contribution is entirely negligible compared with the kinetic energy terms S_1 and S_2.

Suppose as before that the surface lies in the plane $x=0$, and let the metal occupy the semi-infinite region for which $x<0$. It is convenient to consider first only the finite interval $-L \leqslant x \leqslant L$. The energy of the double layer is the sum of the self energy of the negative charge cloud, that of the positive cloud, and the interaction energy of the two, less the same quantity for a uniform neutral distribution confined to $x<0$.

The distribution of positive charge is unaltered and given by

$$\rho_+(x)=\rho_0, \qquad x<0; \qquad\qquad \rho_+(x)=0, \qquad x>0. \qquad \ldots\ldots(38)$$

Thus its self energy is invariable and need not be considered. The energy of any arbitrary charge distribution may be referred to a standard state (zero of energy) which may be fixed arbitrarily. We find it most convenient to take the standard state to be that in which all the negative charge is concentrated in a surface layer at $x=0$. Then the potential energy between the negative charge in (x_1, x_1+dx_1) and that in $(x_2-x_2+dx_2)$ is

$$-2\pi\rho(x_1)\rho(x_2)\,dx_1\,dx_2\,|x_1-x_2| \qquad \ldots\ldots(39)$$

per unit area. For $\rho(x_1)\,dx_1$ is the surface density in the infinite layer of thickness dx_1 at x_1, and so $2\pi\rho(x_1)\,dx_1\rho(x_2)\,dx_2$ is the constant repulsive force exerted on the charge in unit area of the layer between x_2 and x_2+dx_2, while $|x_1-x_2|$ gives the distance of separation. Similar reasoning shows that the potential energy due to the interaction of a layer of positive charge in the interval (x_1, x_1+dx_1) and the negative charge in $(x_2-x_2+dx_2)$ is

$$-2\pi x_1\rho_+(x_1)\rho(x_2)\,dx_1\,dx_2-2\pi|x_1-x_2|\,\rho_+(x_1)\rho(x_2)\,dx_1\,dx_2 \qquad \ldots\ldots(40)$$

per unit area. Here the first term gives the work done to bring the negative charge $\rho(x_2)\,dx_2$ from $x=0$ to $x=x_1$, which is clearly negative. The second term gives the work done to separate it again from the positive charge by a distance $|x_1-x_2|$, which is always positive. The total energy Σ is obtained by combining (39) and (40) and integrating over the various pairs of elements.

$$\Sigma=\pi\int_{-L}^{L} dx_1\int_{-L}^{L} dx_2\{|x_1-x_2|\,[-\rho(x_1)\rho(x_2)-2\rho_+(x_1)\rho(x_2)]-2x_1\rho_+(x_1)\rho(x_2)\}. \qquad \ldots\ldots(41)$$

For the uniform distribution we have simply

$$\rho(x)=-\rho_+(x).$$

Let $\rho'(x)=-\rho_+(x)+\Delta\rho(x)$ be the density of the double layer distribution determined above. The energy of the double layer is then

$$\begin{aligned}S_3=\pi\int_{-L}^{L} dx_1\int_{-L}^{L} dx_2\,|x_1-x_2|\,\{&\rho_+(x_1)\Delta\rho(x_2)+\rho_+(x_2)\Delta\rho(x_1)+\rho_+(x_1)\rho_+(x_2)\\&-2\rho_+(x_1)\Delta\rho(x_2)-\Delta\rho(x_1)\Delta\rho(x_2)-\rho_+(x_1)\rho_+(x_2)\}\\=-\pi\int_{-L}^{L} dx_1\int_{-L}^{L} dx_2\,&|x_1-x_2|\,\Delta\rho(x_1)\Delta\rho(x_2).\end{aligned}$$

The second term of (41) drops out directly on forming the difference since the total negative charge $\int \rho(x_2)\,dx_2$ is the same in each of the two cases. Since $\Delta\rho(x)$ diminishes exponentially in both directions we may pass to the limit $L \to \infty$ and find

$$S_3 = -\pi \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \,|\, x_1 - x_2 \,|\, \Delta\rho(x_1)\Delta\rho(x_2). \qquad \ldots\ldots(42)$$

For $x>0$, $\Delta\rho(x)$ is the density of electronic charge which we have called $-\boldsymbol{e}\sigma_2(x)$. According to (19), it can be represented approximately by the exponential function $-\boldsymbol{e}C\exp(-qx)$. For $x<0$, $\Delta\rho(x)$ is the net charge density $\sigma_1\boldsymbol{e}$ defined by (12) which may be written

$$\sigma_1\boldsymbol{e} \simeq \frac{3\boldsymbol{e}}{4\pi r_0^3}\left[\tfrac{3}{2} A \exp\left(\sqrt{\tfrac{3}{2}}\, x\right)\right], \qquad \ldots\ldots(43)$$

where we have neglected the term in A^2. In the cases considered in the Table the inaccuracy thus introduced is of the order of 1% only. Thus we may write

$$\Delta\rho(x) = Q_2 \exp(-q_2 x), \quad x>0; \qquad \Delta\rho(x) = Q_1 \exp(+q_1 x), \quad x<0, \qquad \ldots\ldots(44)$$

where
$$Q_2 = -\frac{16\pi\boldsymbol{e}}{15}\left(\frac{P_{\mathrm{m}}}{\boldsymbol{h}}\right)^3 \frac{P_{\mathrm{m}}^2}{2\boldsymbol{m}\phi}, \qquad Q_1 = \frac{9\boldsymbol{e}}{8\pi r_0^3} A,$$

$$q_1 = \sqrt{(\tfrac{3}{2})}\,(r_0 E_{\mathrm{F}}/3\boldsymbol{e}^2)^{-\frac{1}{2}} r_0^{-1} \quad \text{and} \quad Q_2/q_2 = -Q_1/q_1. \qquad \ldots\ldots(45)$$

The integration in (42) can then be carried out, giving

$$S_3 = \frac{61600 A^2}{V}\left(\frac{0{\cdot}528}{10^8 r_0}\right)^{3/2}\left(1 + \frac{15\lambda}{4 g_0^{5/2}} A\right) \qquad \ldots\ldots(46)$$

where P_{m} is eliminated using the equation $P_{\mathrm{m}}^2/2\boldsymbol{m} = g_0 E_{\mathrm{F}}$ and V, r_0 are respectively the volume per mole and effective atomic radius in the metal.

The total electronic contribution to the surface energy of the metal is thus given by the sum of the three terms $S = S_1 + S_2 + S_3$ where S_1, S_2, S_3 are given respectively by (30), (37) and (46).

Only S_3 involves a quantity which cannot be explicitly given, namely A, which depends on the solution of (17), and determines the value of the electrostatic potential at the boundary, (10), (16). However, we find (see Table 1) that S_3 is only of the order of a few ergs, which is in fact less than the error to be expected from a simple model.

(iv) *Other Terms*

A contribution to the surface energy from the repulsive interaction of the closed electron shells of the metal ions is to be expected.

This interaction, which is well represented by a central force, would according to Shuttleworth contribute about half as much to the surface free energy per atom as to the binding energy. Thus if it contributes a rather small fraction to the cohesion, it will in the monovalent metals contribute between three and four times that fraction of the surface energy. This is negligible both for the bulky alkali metals and for the noble metals with their hard completed d-shells (Fuchs 1936, Huntington and Seitz 1942).

A more important effect is the change in character of the lattice vibrations of the metal in the presence of a free surface. Brager and Schuchowitzky (1946 b) have considered an extension of the Debye model of a crystal to a large thin sheet of material with free boundaries, and obtain a term proportional to the total surface area in the thermal energy. This surface internal energy due to the lattice vibrations is given by them as

$$E_s = \frac{2\cdot15\,\boldsymbol{k}T}{v^{2/3}}\,\frac{1}{x^2}\left[2\int_0^x \frac{u^2du}{e^u-1} - \frac{x^3}{e^x-1}\right] \text{ ergs/cm}^2, \qquad \ldots\ldots(47)$$

where $x=\Theta/T$ and Θ is the Debye characteristic temperature of the material.

The corresponding value of the free energy is

$$F_s = E_s - T\int_0^T T^{-1}(dE_s/dT)\,dT$$

which can be reduced to

$$F_s = -A_m Z(\Theta/T) \qquad \ldots\ldots(48)$$

where $A_m = 2\cdot15\boldsymbol{k}\Theta/v^{2/3}$ and $Z(x)=x^{-3}\int_0^x \frac{u^2du}{e^u-1}$, so that A_m is a constant for each metal determined by the Debye characteristic temperature and the atomic volume.

The integral occurring in the function Z has previously been tabulated (Zanstra 1931), but only for rather large intervals of the argument. Since $Z(x)$ varies as $1/x$ for small x, it was decided to recalculate the integral and Z. The results are shown in Table 2.

Table 2. $I(x)=\int_0^x \frac{u^2du}{e^u-1}$; $Z(x)=x^{-3}I(x)$

x	$I(x)$	$Z(x)$	x	$I(x)$	$Z(x)$	x	$I(x)$	$Z(x)$
0·1	0·004 835	4·835	0·4	0·069 865	1·092	0·7	0·192 808	0·562
0·12	0·006 916	4·003	0·42	0·076 498	1·033	0·72	0·202 558	0·543
0·14	0·009 351	3·408	0·44	0·083 381	0·979	0·74	0·212 471	0·524
0·16	0·012 131	2·962	0·46	0·090 507	0·930	0·76	0·222 543	0·507
0·18	0·015 250	2·615	0·48	0·097 871	0·885	0·78	0·232 767	0·491
0·2	0·018 700	2·338	0·5	0·105 465	0·844	0·8	0·243 139	0·475
0·22	0·022 474	2·111	0·52	0·113 283	0·806	0·82	0·253 654	0·460
0·24	0·026 565	1·922	0·54	0·121 321	0·771	0·84	0·264 307	0·446
0·26	0·030 966	1·762	0·56	0·129 572	0·738	0·86	0·275 093	0·433
0·28	0·035 670	1·625	0·58	0·138 030	0·707	0·88	0·286 008	0·420
0·3	0·040 668	1·506	0·6	0·146 689	0·679	0·9	0·297 046	0·408
0·32	0·045 956	1·403	0·62	0·155 543	0·653	0·92	0·308 204	0·396
0·34	0·051 527	1·311	0·64	0·164 588	0·628	0·94	0·319 477	0·385
0·36	0·057 373	1·230	0·66	0·173 817	0·605	0·96	0·330 859	0·374
0·38	0·063 488	1·157	0·68	0·183 226	0·583	0·98	0·342 348	0·364

It should be noted that the contribution to the total surface free energy from this source is negative.

This calculation of the surface free energy due to lattice vibrations is, of course, only valid for the crystalline solid. For the liquid, consideration of capillary waves (Frenkel 1946) provides the most reasonable approach, but in the absence of a more detailed theory of liquid structure such considerations cannot be subjected to quantitative test.

We have therefore calculated, for approximate comparison with the experimental results for the surface tension of the liquid metals near their melting points, the total surface free energies of the solid metals at their melting points, using the expression

$$\begin{aligned}\sigma &\simeq S_1+S_2+F_s\\ &=\frac{1{\cdot}44\times10^5}{V^{4/3}}\left\{\frac{\pi}{8}-\frac{1}{16}\left[3(2-\lambda)\sqrt{(\lambda-1)}+(3\lambda^2-8\lambda+8)\sin^{-1}\sqrt{\left(\frac{1}{\lambda}\right)}\right]\right)\\ &\quad-2{\cdot}11(\Theta/V^{2/3})Z(\Theta/T_{\mathrm{m}})\ \mathrm{ergs/cm^2} \qquad \ldots\ldots(49)\end{aligned}$$

where V is the mole volume in cubic centimetres and Θ, T_{m} the Debye characteristic temperature and melting point respectively in degrees absolute. λ is the ratio of the barrier height ϕ to the maximum Fermi energy E_{F}.

§ 6. NUMERICAL RESULTS

Theoretical work on the noble and alkali metals has shown that the conduction electrons of these metals behave almost like free electrons. Thus we can use the ordinary electron mass in our calculation, so that the electronic contribution to the surface energy depends only on the height of the potential barrier ϕ and the mole volume V. The estimate of ϕ most consonant with the model we employ is obtained from the consideration that the binding energy W of the metal (atomic ionization energy plus heat of sublimation) is related to ϕ by the equation (Huang 1948)

$$-W=\sum_i\left(-\phi+\frac{\hbar^2k_i^2}{2m}\right)=N\left(\tfrac{3}{5}E_{\mathrm{F}}-\phi\right). \qquad \ldots\ldots(50)$$

The calculated values of the various terms in the surface energy and the strength of the double layer for the noble and alkali metals are given in Table 1, together with the experimental values used in the calculation. The experimental values of the surface energies of the liquid metals as given in Brager and Schuchowitzky (1946) are given in the Table for comparison.

The agreement with the theoretical values is within a factor of about 1·5, which is as much as can reasonably be expected from this model. The relative values for different metals agree well. There are no definite experimental values for the double layer moments, but the values found are in substantial agreement with more elaborate theoretical calculations obtained (Bardeen 1936) in this theory of the work function.

One might notice that the differences $(\phi-E_{\mathrm{F}})$ formed from the values of ϕ and E_{F} given in Table 1 are much higher than the experimental values for the work functions of the same metals. This discrepancy is, however, only apparent. It is a consequence of the fact that we have used a single barrier height ϕ for all electrons, whereas in reality different electrons have effectively different barriers owing to the difference in the exchange correlation energy $-\epsilon(k)$ for electrons with different wave number k (cf. Seitz 1940). Thus the effective barrier for an electron with wave number k is higher than that for an electron at the top of the Fermi distribution (wave number k_0), by $\epsilon(k)-\epsilon(k_0)$. If χ is the observed work function, so that the barrier for an electron at the top of the distribution is $\phi(k_0)=\chi+E_{\mathrm{F}}$, the effective barrier for an electron with wave number k is $\phi(k)=\chi+E_{\mathrm{F}}+\epsilon(k)-\epsilon(k_0)$. The mean value for all electrons is

$$\bar{\phi}=\chi+E_{\mathrm{F}}+\bar{\epsilon}-\epsilon(k_0)=\chi+E_{\mathrm{F}}+0{\cdot}916\boldsymbol{e}^2/r_0-0{\cdot}712\boldsymbol{e}^2/r_0 \qquad \ldots\ldots(51)$$

where the expressions for $\bar{\epsilon}$, $\epsilon(k_0)$ are from Seitz (1940).

If the mean barrier heights thus determined are used in the calculation, results for the surface energy are obtained which differ only very slightly from those given in Table 1.

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The Emission Spectrum of Sodium Hydride

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ABSTRACT. Observations on the spectrum of sodium hydride have been extended to longer wavelengths (from 4600 A. to 6450 A.) and photographed under high dispersion. Analysis of the data thus obtained gives values of the vibrational and rotational constants for several new vibrational levels, among which the lowest levels of the excited state are of especial interest.

The intensity distribution has been calculated from the wave functions appropriate to potential energy curves based on the constants derived from the analysis of the band system. The theoretical estimates are found to be in fair agreement with the experimental results.

§ 1. INTRODUCTION

The absorption spectrum of sodium hydride was reported by Hori in 1930. The values assigned to v' were subsequently raised by one unit as a result of work on the emission spectrum (Hori 1931), and later by a further three units on the basis of a comparison with the deuteride (Olsson 1934).

No data were available for these lowest three vibrational levels of the excited state. They are of especial interest because the values of ω_v' and B_v' for the hydrides of the alkali metals behave anomalously in that they first increase with

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v' instead of decreasing throughout. The present work was undertaken with a view to determining the missing data; the preliminary results have been reported elsewhere (Pankhurst 1941).

§ 2. EXPERIMENTAL

The spectrum was obtained from a hydrogen discharge tube source of the type described by Pearse and Gaydon (1938), the discharge passing through a quartz constriction containing a pellet of sodium. The tube was cooled by immersion in water, a current of from 0·3 to 1·0 amp. being supplied from a 2,500 v. transformer.

The band system was photographed with 6-m. gratings, using Ilford H.P.2 and hypersensitive panchromatic plates. Between 4600 A. and 5660 A. a dispersion of 1·9 A/mm. was obtained by means of the second order of a grating with 11,000 lines/inch (433 per mm.); further to the red the first order of a grating with 15,000 lines inch (591 per mm.) was employed, giving a dispersion of 2·6 A/mm. The whole system was also photographed on a Hilger E2 quartz prism spectrograph.

§ 3. ANALYSIS OF EXPERIMENTAL RESULTS

The system is of the many-line type, with no apparent band-heads. It arises from a ${}^1\Sigma$–${}^1\Sigma$ transition and resolves, on analysis, into R– and P– branches. Some 25 new bands were identified, involving transitions from seven vibrational levels. (A copy of the detailed rotational analysis of each band may be seen on application to the author.)

Rotational and Vibrational Analysis. Mean values of the observed combination differences, obtained by averaging the values for all the bands obtained from each of the vibrational energy-levels, are set out in Table 1. The rotational analysis was based on the usual power-series representation of the rotational energy, the constants thus derived being given at the foot of the Table. The closeness to which the experimental results are represented is shown by the agreement between the observed combination differences and those calculated from the derived rotational constants: the agreement is everywhere well within the probable error of the observations.

The vibrational analysis is set out in Table 2, which includes Hori's (1931) values for bands involving transitions to the lowest three levels of the ground state. The vibrational energy in each of the two electronic states is represented by the power-series expressions for $G(v+\frac{1}{2})$ given in the Table. The accuracy to which these expressions fit the experimental data is indicated by the agreement of the calculated band-origins included in Table 2.

Note on Accuracy. It is important not to claim high accuracy for the absolute values of constants obtained as coefficients in power-series expansions such as those for $F(K)$, $B_v(u)$, $D_v(u)$, $H_v(u)$ and $\omega_v(u)$, because a substantial alteration to any one of the coefficients can be largely compensated for by appropriate adjustments of the others. It is in fact possible to find several polynomials of the same degree but with corresponding coefficients considerably different, both of which represent the original observations to within the experimental error. Although this may be immaterial if a power series is to be used merely for the purpose of interpolation, it introduces considerable uncertainty when (as in this present case) the coefficients are to be interpreted as physical properties of the system.

Table 1. Rotational Analysis

(*a*) *Excited State*

(i) Mean values of the observed combination differences, $\Delta_2'(K) = \mathrm{R}(K) - \mathrm{P}(K)$

K \ v'	1	2	3	4	5	6	7
1	11·85	10·86	11·52	11·69		12·23	
2	18·46	18·68	19·42	19·33		19·77	19·38
3	25·22	26·16	26·87	26·94		27·43	27·17
4	32·66	33·61	34·20	34·57	34·84	34·89	34·68
5	39·47	40·91	41·60	42·17	42·43	42·25	42·37
6	46·84	48·26	49·13	49·68	49·95	50·06	50·02
7	54·00	55·54	56·46	57·15	57·49	57·55	57·43
8	60·94	62·67	63·82	64·57	64·79	64·99	64·91
9	67·76	69·72	71·06	71·81	72·37	72·33	72·25
10	74·54	76·70	78·17	79·10	79·55	79·68	79·56
11	81·21	83·59	85·19	86·14	86·60	86·87	86·72
12	87·82	90·31	92·07	93·16	93·66	93·94	93·87
13	94·23	96·94	98·76	100·03	100·70	100·96	100·85
14	100·63	103·46	105·37	106·80	107·49	107·74	107·67
15	106·88	109·83	112·00	113·41	114·17	114·49	114·38
16	113·00	116·18	118·38	119·90	120·68	120·84	121·06
17	118·97	122·19	124·67	126·29	127·13	127·51	127·56
18	124·84	128·22	130·67	132·46	133·50	133·95	133·83
19	130·65	134·10	136·69	138·44	139·50	140·03	139·97
20	136·42	139·76	142·47	144·24	145·42	145·98	145·97
21	141·75	145·40	148·11	150·21	151·29	151·96	151·78
22	147·12	150·75	153·66	155·63	156·97	158·18	157·42
23	152·28	156·16	159·12	161·15	162·38		162·79
24	157·54	161·37	164·33	166·42	167·71		168·26
25	162·70	166·37	169·31	171·49	172·73		172·95
26	167·60	171·29	174·24	176·46	178·01		
27		176·13	179·06	181·36	182·70		
28		180·80	183·73		187·50		
29		185·32	188·20		191·92		
30		189·33	192·61		196·10		
31			196·90				

(ii) Values derived for the rotational constants (in cm^{-1})

v'	1	2	3	4	5	6	7
B_v'	1·823	1·875	1·908	1·930	1·938	1·941	1·936
$D_v' \times 10^4$	−2·25	−2·25	−2·20	−2·19	−2·07	−2·01	−1·93
$H_v' \times 10^8$	5·10	3·85	3·04	2·87	2·02	1·5–	1·24

$$F_v'(K) = B_v'K(K+1) + D_v'K^2(K+1)^2 + H_v'K^3(K+1)^3.$$

The above constants may be represented by the equations :

$$B_v' = B_e' + \alpha_1'u' + \alpha_2'u'^2 + \ldots . \qquad (u' - v' + \tfrac{1}{2})$$
$$D_v' = D_e' + \beta_1'u' + \beta_2'u'^2 + \ldots .$$
$$H_v' = H_e' + \gamma_1'u' + \gamma_2'u'^2 + \ldots .$$

with the following values of the coefficients :

$B_e' = 1{\cdot}696$, whence $I_e' = 16{\cdot}31 \times 10^{-40}$ gm.cm^2 and $r_e' = 3{\cdot}200$ A. ; $\alpha_1' = 0{\cdot}1083$; $\alpha_2' = -0{\cdot}0175$; $\alpha_3' = 0{\cdot}00129$; $\alpha_4' = 0{\cdot}000042$; $D_e' = -2{\cdot}27 \times 10^{-4}$; $\beta_1' = -0{\cdot}01 \times 10^{-4}$; $\beta_2' = 0{\cdot}008 \times 10^{-4}$; $H_e' = 5{\cdot}7 \times 10^{-8}$; $\gamma_1' = -0{\cdot}65 \times 10^{-8}$.

Table 1 (*cont.*)

(*b*) *Ground State*

(i) Mean values of the observed combination differences, $\Delta_2''(K) = \mathrm{R}(K-1) - \mathrm{P}(K+1)$

K \ v''	3	4	5	6	7	8
1	26·45	24·90	25·71			
2	44·33	42·50	42·07	41·33	39·27	
3	61·98	60·22	58·39	56·70	54·70	
4	79·62	77·24	74·96	72·58	70·46	
5	97·13	94·32	91·48	88·60	85·83	83·01
6	114·63	111·15	107·98	104·62	101·14	97·94
7	131·96	128·06	124·30	120·34	116·59	112·66
8	149·24	144·76	140·45	136·12	131·74	127·30
9	166·41	161·37	156·53	151·83	146·94	141·77
10	183·27	177·84	172·50	167·16	161·77	156·45
11	200·10	194·15	188·27	182·41	176·62	170·69
12	216·73	210·35	203·84	197·49	191·27	184·73
13	233·14	226·23	219·32	212·46	205·70	198·74
14	249·40	241·93	234·63	227·20	219·84	212·52
15	265·49	257·57	249·68	241·78	233·93	226·05
16	281·31	272·81	264·49	256·10	247·77	239·36
17	296·76	288·02	278·97	270·19	261·34	252·43
18	312·17	302·78	293·36	284·03	274·71	265·35
19	327·24	317·26	307·60	297·57	287·77	277·99
20	342·03	331·61	321·24	310·93	300·62	290·22
21	356·41	345·52	334·77	—	313·17	
22	370·70	359·40	348·10	336·84	325·35	
23	384·61	372·82	360·98	349·45	337·51	
24	398·25	385·92	373·71	361·15		
25	411·55	398·68	386·02			
26	424·45	411·13	398·07			
27	437·15	423·30	409·65			
28	449·32	435·10	421·00			
29	461·10	447·28	432·01			
30	472·63	—	442·63			
31	483·79	468·72	452·75			

(ii) Values derived for the rotational constants (in cm^{-1})

v''	3	4	5	6	7	8
B_v''	4·438	4·302	4·180	4·051	3·919	3·790
$D_\mathrm{v}'' \times 10^4$	−3·31	−3·13	−3·29	−3·25	−3·05	−3·04
$H_\mathrm{v}'' \times 10^8$	2·17	1·13	2·58	2·70	0·69	1·10

$$F_\mathrm{v}''(K) = B''K(K+1) + D_\mathrm{v}''K^2(K+1)^2 + H_\mathrm{v}''K^3(K+1)^3.$$

The variation of B_v'' may be represented by the equation $B_\mathrm{v}'' = B_\mathrm{e}'' + \alpha_1''u''$, $(u'' = v'' + \tfrac{1}{2})$, with $B_\mathrm{e}'' = 4{\cdot}886$, whence $I_\mathrm{e}'' = 5{\cdot}66 \times 10^{-40}$ gm.cm^2 and $r_\mathrm{e}'' = 1{\cdot}885$ A.; $\alpha_1'' = -0{\cdot}129$. Mean value of $D_\mathrm{v}'' = -3{\cdot}15 \times 10^{-4}$; mean value of $H_\mathrm{v}'' = 1{\cdot}7 \times 10^{-8}$.

Energy of Dissociation. The usual equation

$$\mathbf{D} = -\omega_e^2/4x_e\omega_e \qquad \ldots\ldots(1)$$

assumes a regular closing up of the vibrational energy levels. For NaH this condition is satisfied in the ground state but not in the excited state, for which ω_v at first increases with v. The above equation was therefore used only for the ground state; the value for the excited state was obtained from that for the ground state by assuming that the products of dissociation were a normal sodium atom and a normal hydrogen atom from the ground state, and an excited (^{2}P) sodium atom and a normal hydrogen atom from the excited state. The results were:

$$\mathbf{D}' = 11{,}650 \text{ cm}^{-1} = 1{\cdot}44 \text{ ev.}; \qquad \mathbf{D}'' = 17{,}410 \text{ cm}^{-1} = 2{\cdot}16 \text{ ev.}$$

§ 4. POTENTIAL ENERGY CURVES, WAVE FUNCTIONS AND INTENSITY DISTRIBUTION

In order to estimate the intensity distribution by the methods of wave mechanics it is first necessary to determine the potential energy curves for the two electronic states and then to calculate the wave functions for all the vibrational levels. If ψ' and ψ'' denote wave functions for the excited state and the ground state respectively, the intensity of each band (v', v'') is obtained from the expression $\int(\psi'\bar{\psi}'' + \bar{\psi}'\psi'')\,dr$, where the bars denote complex conjugates.

Excited State. The potential energy in the excited state was written in the form

$$V'(r) = a_0'\xi'^2(1 + a_1'\xi' + a_2'\xi'^2 + \ \ldots\ldots) \qquad \ldots\ldots(2)$$

where

$$\xi' = (r - r_e')/r_e', \qquad \ldots\ldots(3)$$

with the coefficients evaluated from the vibrational and rotational constants using the expressions given by Dunham (1932) but neglecting the small correction terms of the order B_e^2/ω_e^2. The values obtained were:

$$a_0' = 14{,}220 \text{ cm}^{-1}; \qquad a_1' = 0{\cdot}949; \qquad a_2' = 3{\cdot}25; \qquad a_3' = -7{\cdot}09.$$

The resulting potential curve lay entirely within the parabola $a_0'\xi'^2$ and resembled another parabola of smaller latus rectum. This observation was exploited when calculating the wave functions ψ' (§ 5). For most molecules the right-hand limb of the potential curve falls below the simple parabola; the irregularity in this instance is associated with the anomalous behaviour of the constants for the excited state.

Ground State. In the ground state the potential curve given by a similar power series flattens prematurely, for positive values of ξ, between $v'' = 4$ and $v'' = 5$. As dissociation could not have taken place at these values of v'', it was concluded that an expression of the form of equation (2) is not suitable for representing the potential energy of NaH in the ground state.

The expression due to Morse (1929) was therefore used instead:

$$V_M(r) = \mathbf{D}[1 - e^{-a(r-r_e)}]^2 \qquad \ldots\ldots(4)$$

with $\mathbf{D}'' = 17{,}410$ cm^{-1} and $a'' = 1{\cdot}070$ A^{-1}.

Intensity Distribution. The intensity of the band $v' \rightarrow v''$ is

$$I(v', v'') = C \exp\{-\boldsymbol{hc}G'(v')/\boldsymbol{k}T\}\nu_0^4\left[\int_0^\infty (\psi'\bar{\psi}'' + \bar{\psi}'\psi'')\,dr\right]^2 \qquad \ldots\ldots(5)$$

where C is an arbitrary constant, $\boldsymbol{k}$ the gas constant per molecule and T the absolute temperature.

Table 2. Vibrational Scheme

v' \ v''	0	1	2	3	4	5	6	7	8	Mean $\Delta G'$	v'
1	—	—	—	—	—	17324·4(948·8) [17323·9] (329·9)	16375·6 [16375·3] (330·0)	—	—	329·9	1
2	—	—	—	19659·8(1021·2) [19659·0] (337·1)	18638·6(984·3) [18638·2] (337·2)	17654·3(948·7) [17653·7] (337·2)	16705·6 [16705·1]	—	—	337·2	2
3	23282·8(1132·9) [23282·6] (343·8)	22149·9(1094·5) [22149·4] (343·6)	21055·4(1058·5) [21054·2] (343·4)	19996·9(1021·1) [19996·6] (343·9)	18975·8(984·3) [18975·7] (343·7)	17991·5 [17991·2]	—	16130·1 [16129·9] (343·6)		343·7	3
4	23626·6(1133·1) [23626·8] (349·4)	22493·5(1094·7) [22493·6] (349·3)	21398·8(1058·0) [21398·5] (349·4)	20340·8(1021·3) [20340·8] (349·9)	19319·5 [19319·9] (350·0)	—	17386·6(912·9) [17386·9] (349·6)	16473·7 [16474·1] (349·7)	—	349·6	4
5	23976·0(1133·2) [239·765] (353·8)	22842·8(1094·6) [22843·3] (354·0)	21748·2(1057·5) [21748·1] (354·0)	20690·7(1021·2) [20690·5]	19669·5(984·5) [19669·6] (353·7)	18685·0(948·8) [18685·1] (353·8)	17736·2(912·8) [17736·6]	16823·4(877·0) [16823·8]	15946·4 [15946·6] (354·1)	353·9	5
6	24329·8(1133·0) [24330·5] (357·4)	23196·8(1094·6) [23197·2] (357·7)	22102·2 [22102·1] (357·4)	—	20023·2(984·4) [20023·6] (357·2)	19038·8 [19039·1] (357·2)	—	—	16300·5 [16300·6] (357·2)	357·4	6
7	24687·2(1132·7) [24687·6] (359·4)	23554·5(1094·9) [23554·4] (358·9)	22459·6 [22459·2] (359·3)	—	20380·4(984·4) [20380·7]	19396·0 [19396·2]	—	17534·6(876·9) [17534·9]	16657·7 [16657·7]	359·2	7
8	25046·6(1133·2) [25046·8] (360·0)	23913·4(1094·5) [23913·5] (360·6)	22818·9 [22818·4]							360·3	8
9	25406·6(1132·6) [25407·0] (360·2)	24274·0 [24273·7] (360·0)								360·1	9
10	25766·8(1132·8) [25767·2] (359·5)	24634·0 [24633·9] (359·5)								359·5	10
11	26126·3(1132·8) [26126·5] (357·7)	24993·5 [24993·3]								357·7	11

The entries without brackets are the wave-numbers of the band-origins obtained from the rotational analysis : their differences are given between round brackets. The numbers in square brackets correspond to the equation

$$\nu=\nu_0+G'(u')-G''(u''),$$

with

$$G'(u')=\omega_e'u'+x_e'\omega_e'u'^2+y_e'\omega_e'u'^3+\ldots.$$
$$=310{\cdot}6u'+5{\cdot}41u'^2-0{\cdot}197u'^3-0{\cdot}00073u'^4+0{\cdot}000073u'^5,$$
$$G''(u'')=\omega_e''u''+x_e''\omega_e''u''^2+y_e''\omega_e''u''^3+\ldots.$$
$$=1172{\cdot}2u''-19{\cdot}72u''^2+0{\cdot}160u''^3-0{\cdot}005u''^4$$

and

$$\nu_0=22719{\cdot}1\ (\text{cm}^{-1}).$$

12	26484·0 [26484·1] (354·3)		—							354·3	12
13	26838·3 [26839·2] (352·3)		—							352·3	13
14	27190·6 [27191·1] (348·6)	(1132·9)	26057·7 [26057·8] (348·3)							348·4	14
15	27539·2 [27539·2] (343·6)	(1133·2)	26406·0 [26406·0] (344·3)							343·9	15
16	27882·8 [27883·1] (340·0)	(1132·5)	26750·3 [26749·9] (340·0)							340·0	16
17	28222·8 [28222·5] (334·1)	(1132·5)	27090·3 [27089·3] (333·4)							333·7	17
18	28556·9 [28557·0] (330·1)	(1133·2)	27423·7 [27423·8] (330·0)							330·0	18
19	28887·0 [28886·7] (323·7)	(1133·3)	27753·7 [27753·5]							323·7	19
20	29210·7 [29211·6]										20
Mean ΔG''		1132·9	1094·6	1058·0	1021·2	984·4	948·8	912·8	876·9		

Table 3 *a*. Observed Intensity Distribution

v' \ v''	3	4	5	6	7	8
0						
1			3	**3**		
2	3	4	**4**	**3**		
3	**5**	**6**	**5**		1	
4	**5**	3			**3**	
5	3	1	2	**3**	2	1
6		3	**5**			**3**
7		**4**	3		**4**	2
8						

Table 3 *b*. Calculated Intensity Distribution

v' \ v''	3	4	5	6	7	8
0	4	13	31	49	**62**	**90**
1	25	60	**99**	**95**	**71**	62
2	61	**100**	**96**	50	8	1
3	**75**	70	32	0	10	**16**
4	55	21	0	**16**	**20**	9
5	15	0	**9**	9	3	0
6	0	**13**	**9**	0	3	**3**
7	5	**11**	1	**4**	**6**	1
8	**7**	3	1	**5**	1	0

§ 5. COMPUTATIONAL DETAILS

Excited State. As an analytical solution was not available for the wave functions appropriate to a power-series potential curve, they were obtained for the excited state by modifying those for the parabola $a_0'\xi'^2$, for which the solution may be written $\psi = bF(\mathrm{v}, \mathrm{r})$ where $b^2 = 2\pi\sqrt{(\mu \mathbf{c}\omega_e/\boldsymbol{h})}$ and

$$F(\mathrm{v}, \mathrm{r}) = \sqrt{\left(\frac{1}{2^v\, v\,!\sqrt{\pi}}\right)} \exp(-s^2/2) H_{\mathrm{v}}(s),$$

μ being the reduced mass of the molecule, and H_{v} denoting successive Hermitian polynomials with $s = b^2(r - r_e)$.

The modification consisted simply of adjusting the abscissae so as to "fit" the wave functions to the limbs of the power-series curve instead of to the limbs of the parabola. The ordinates for each vibrational level were then multiplied by a constant factor in order to maintain normalization. This procedure, although somewhat crude, is to some extent justified by the resemblance of the power-series potential curve to another parabola of smaller latus rectum (as already noted in § 4), and might be expected to give results at least as accurate as the eye-estimates of the observed intensity distribution. As a check, a parabola was fitted to the power-series curve by the method of least squares; its wave function was evaluated for one vibrational level ($v' = 5$) and was found to agree reasonably well with that obtained by the arbitrary method indicated above.

Ground State. The wave functions corresponding to equation (4) have been derived by Morse (1929) and may be written in the form

$$\psi_{\mathrm{M}} = F_e F_{\mathrm{e,v}} F_{\mathrm{e,v,r}} \qquad \ldots\ldots(6)$$

where

$$F_e = (ka)^{\frac{1}{2}}, \qquad \ldots\ldots(7)$$

$$\boldsymbol{F}_{\mathrm{e,v}} = (N_{\mathrm{v,v}})^{-\frac{1}{2}} \frac{\Gamma(k-v)}{v\,!} \exp\{i\pi(k-v-1)\}, \qquad \ldots\ldots(8)$$

$$F_{\mathrm{e,v,r}} = e^{-z/2} z^{(k-2v-1)/2}\left[z^v - (k-v-1)vz^{v-1} + \frac{(k-v-1)(k-v-2)v(v-1)}{2!} z^{v-2} - \ldots\right] \qquad \ldots\ldots(9)$$

and

$$k = 4\pi(2\mu\mathbf{D})^{\frac{1}{2}}/a\boldsymbol{h}; \qquad z = k\exp\{-a(r-r_e)\}, \qquad \ldots\ldots 10)$$

$$N_{\mathrm{v,v}} = [\Gamma(k-v)]^2 \sum_{p=0}^{v} \Gamma(k-2v+p-1)/\Gamma(p-1). \qquad \ldots\ldots(11)$$

The numerical computation of equations (6) to (11) would involve a prohibitive amount of labour, partly owing to the large number of points needed to define the wave curves for the higher vibrational levels, and partly because each term in equation (9) has to be evaluated to extremely high accuracy in order to obtain relatively few significant figures in the sum, since the positive and negative terms are so nearly equal and opposite. Equation (6) was therefore evaluated for only three of the levels (namely $v'' = 0$, 4 and 6) and an approximate method was devised for circumventing the numerical evaluation of equation (6) for the other vibrational levels.

This approximate method is suggested by the observation that if the exponential in equation (4) is expanded in series, the first term is of the form $a_0\xi^2$, for which the wave functions can more readily be obtained. For the remaining levels of the ground state, therefore, wave functions were first calculated for the simple parabola and then modified in a manner similar to that adopted for the excited state. Normalization was preserved by scaling the ordinates by the constant factor appropriate to each vibrational level. The method was justified by a comparison of the values of $(\psi'\bar{\psi}'' + \bar{\psi}'\psi'')$ (cf. equation (12) below) with those obtained from the exact solutions for $v'' = 0$, 4 and 6.

Intensity Distribution. With the potential energy curves of equations (2) and (4),

$$\psi'\bar{\psi}'' + \bar{\psi}'\psi'' = \psi'\chi'', \qquad \ldots\ldots(12)$$

where $\chi'' = F''_{\mathrm{e}} F''_{\mathrm{e,\,v}} F''_{\mathrm{e,\,v,\,r}}$ with F''_{e} and $F''_{\mathrm{e,\,v,\,r}}$ given by (7) and (9) but with

$$F''_{\mathrm{e,\,v}} = 2(N''_{\mathrm{v,\,v}})^{-\frac{1}{2}} \frac{\Gamma(k'' - v'')}{v''!} \cos(k'' - v'' - 1)\pi. \qquad \ldots\ldots(8a)$$

In evaluating equation (5), a temperature of 680° C. was assumed, corresponding to a value of 1·5 for $\boldsymbol{hc}/\boldsymbol{k}T$. This assumed temperature may be a little high, but will not materially affect the general comparison with the experimental results. The arbitrary constant C was so chosen as to give values of intensity on a scale of 100 for the strongest band.

§ 6. THEORETICAL RESULTS

The calculated intensity distribution is compared with the experimental eye-estimates in Table 3 (inset in Table 2). The theoretical values show the three observed loci of maximum intensity indicated by heavy type in the Deslandres array. Moreover, the positions of these loci are given with fair accuracy, despite the high values of v' and v'' at which the secondary maxima occur, where the approximate wave functions used might be expected to be least reliable. In view of the several approximations introduced in the numerical work, and the various assumptions involved in the basic theory, the general agreement with the observed intensities is surprisingly good.

The trend of the primary (Franck–Condon) locus of maximum intensity for small values of v' explains completely the drastic extension of the spectrum which had proved to be necessary in order to obtain bands involving transitions from the lower vibrational levels of the excited state.

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Bending Vibrations of a Linear Chain

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ABSTRACT. The bending frequencies of a linear chain of n mass points have been calculated using a harmonic potential function involving forces between second neighbours. The proper boundary conditions are introduced and a general formula for the bending frequencies is derived.

THE longitudinal vibrations in a linear chain consisting of equidistant mass points held together by quasi-elastic forces have been known for some time although no attempts have been made to compute the bending frequencies of a linear chain containing a finite number of mass points. In the case of a continuous distribution of mass points, this case passes into the case of the transverse oscillations of an infinitely thin rod.

The linear chain will be assumed to consist of n equidistant mass points of mass m which are held together by valence and angle forces, i.e. forces between immediate and second neighbours. The potential function V, assumed to be harmonic, of such a chain will then be

$$2V = f \sum_{i=1}^{n-1} l_i^2 + a^2\phi \sum_{i=2}^{n-1} \lambda_i^2, \qquad \ldots\ldots(1)$$

where the l_i are the variations in the distances between P_{i+1} and P_i, the λ_i are the angles between P_{i-1}, P_i and P_{i+1} produced by the oscillations, and a is the equilibrium distance between the mass points. If u_i, v_i are the horizontal and vertical displacements respectively of the vibrating mass points, it is easily seen that

$$l_i = u_{i+1} - u_i; \qquad \lambda_i = (-1)^i(2v_i - v_{i-1} - v_{i+1})/a, \qquad \ldots\ldots(2)$$

assuming that u_i^2 and v_i^2 are very much less than a^2. It follows that the vibrations of such a chain split up into two branches, that of the valence vibrations due to the force f between adjacent masses, and that of the bending frequencies produced by the force ϕ between second neighbours. The valence frequencies arise from the longitudinal displacements of the particles and the bending frequencies from their movements normal to the direction of the chain, in strict analogy to the longitudinal and transverse oscillations of a bar or rod.

The differential equations of the transverse vibrations are, according to (1) and (2)

$$\left.\begin{aligned} -m\ddot{v}_i &= (-1)^i a\phi(2\lambda_i + \lambda_{i-1} + \lambda_{i+1}) \\ \text{or} \qquad -m\ddot{v}_i &= \phi(v_{i-2} - 4v_{i-1} + 6v_i - 4v_{i+1} + v_{i+2}). \end{aligned}\right\} \qquad \ldots\ldots(3)$$

If we write $\Delta^{(1)}v_i = v_{i+1} - v_i$; $\Delta^{(2)}v_i = v_{i+2} - 2v_{i+1} + v_i$ and in general

$$\Delta^{(k)}v_i = \Delta^{(k-1)}v_{i+1} - \Delta^{(k-1)}v_i,$$

the system of equations (3) can be written in the form of difference equations:

$$m\ddot{v}_i = \phi\Delta^{(4)}v_{i+2}, \qquad \ldots\ldots(4)$$

and λ_i becomes $-(-1)^i\Delta^{(2)}v_{i-1}$. Equation (4) is analogous to the differential equation determining the transverse vibrations of a bar $\rho\ddot{y} = -\kappa^2 q(d^4y/dx^4)$ where ρ is the density of the material, y the vertical displacement of the point with the abscissa x, κ the radius of gyration about a line through the axis, and q Young's modulus (Rayleigh 1929). Using the expression (2), the system (4) transforms into

$$-m\ddot{\lambda}_i=\phi(\lambda_{i-2}+4\lambda_{i-1}+6\lambda_i+4\lambda_{i+1}+\lambda_{i+2}). \qquad \ldots\ldots(5)$$

There are $n-2$ simultaneous equations corresponding to the $n-2$ valence angles.

The boundary conditions can now be derived from the equations for the two initial and final angles which have to be evaluated separately from (1) and (2). These equations will be somewhat different from (5) since the points P_1, P_2, P_{n-1} and P_n have not the full complement of second neighbours. There result the equations (6):

$$\left.\begin{array}{ll}-m\ddot{\lambda}_2=\phi(6\lambda_2+4\lambda_3+\lambda_4); & -m\ddot{\lambda}_3=\phi(4\lambda_2+6\lambda_3+4\lambda_4+\lambda_5);\\ -m\ddot{\lambda}_{n-2}=\phi(\lambda_{n-4}+4\lambda_{n-3}+6\lambda_{n-2}+4\lambda_{n-1}); & -m\ddot{\lambda}_{n-1}=\phi(\lambda_{n-3}+4\lambda_{n-2}+6\lambda_{n-1}).\end{array}\right\} \qquad \ldots\ldots(6)$$

These four equations can be said to have the same form as (5) if it is assumed that

$$\left.\begin{array}{ll} & \lambda_0,\ \lambda_1,\ \lambda_n,\ \lambda_{n+1}=0\\ \text{or} & \Delta^{(2)}v_{-1},\ \Delta^{(2)}v_0,\ \Delta^{(2)}v_{n-1},\ \Delta^{(2)}v_n=0\ .\end{array}\right\} \qquad \ldots\ldots(6a)$$

The equations (6*a*) represent the four boundary conditions; they indicate that no force couples act on the two ends of the chain. In the case of the continuous bar they reduce to the conditions that $d^2y/dx^2=0$ for $x=0$ and $x=l$ if the two ends of the bar represented by $x=0$ and $x=l$ are free. λ_r is now assumed to be $\lambda_r=\cos\omega t\{Ae^{ir\alpha}+Be^{-ir\alpha}+(-1)^rCe^{r\beta}+(-1)^rDe^{-r\beta}\}$. If the first three boundary conditions are applied, the following value obtains for λ_i:

$$\begin{aligned}\lambda_i=A'\cos\omega t\{&(-1)^{n+i}\sin\alpha\sinh(n-i)\beta-\sin(n-i)\alpha\sinh\beta\\ &+(-1)^n\sin i\alpha\sinh(n-1)\beta+(-1)^n\sin(i-1)\alpha\sinh n\beta\\ &-(-1)^i\sin n\alpha\sinh(i-1)\beta-(-1)^i\sin(n-1)\alpha\sinh i\beta\}.\end{aligned} \qquad \ldots\ldots(7)$$

The last boundary condition leads to

$$\begin{aligned}0=2\sin\alpha\sinh\beta&+(-1)^n\sin(n+1)\alpha\sinh(n-1)\beta\\ &+(-1)^n\sin(n-1)\alpha\sinh(n+1)\beta+2(-1)^n\sin n\alpha\sinh n\beta.\end{aligned} \qquad \ldots\ldots.(8)$$

The relation between α and β can be determined in the following way: if equation (5) is solved by a term $Aa^i\cos\omega t$ for λ_i, it follows that a is a solution of the equation

$$a^4+4a^3+(6\phi-m\omega^2)a^2/\phi+4a+1=0. \qquad \ldots\ldots(9)$$

If the roots of (9) are a_1, a_2, a_3 and a_4, we have

$$\sum_{i=1}^{4}a_i=-4,\qquad \prod_{i=1}^{4}a_i=1,\qquad \sum_{i=1}^{4}a_i=\sum\sum_{i\neq j\neq k}a_ia_ja_k.$$

These relations are fulfilled if $a_2=1/a_1$, $a_3=1/a_4$. If then $a_1=e^{i\alpha}$, $a_2=e^{-i\alpha}$, it follows that $a_3+1/a_3=-4-2\cos\alpha$. If a_3 is assumed to be $-e^{\beta}$, the relation between α and β is

$$\cosh\beta=2+\cos\alpha. \qquad \ldots\ldots(10)$$

Expression (9) shows that $6\phi-m\omega^2/\phi=\sum_{i\neq j}a_ia_j=2(1-2\cos\alpha\cosh\beta)$, therefore $\omega=2\pi\nu$ can be determined, taking (10) into account:

$$m\omega^2=4\phi(1+\cos\alpha)^2;\qquad \nu=[(1+\cos\alpha)/\pi]\sqrt{(\phi/m)}\quad 0<\alpha<\pi. \qquad \ldots\ldots(11)$$

For every value of n, there are $n-2$ solutions for $\cos\alpha$. All the possible bending frequencies are contained within the limits $\nu_{\min}=0$ and $\nu_{\max}=(2/\pi)\sqrt{(\phi/m)}$. β can assume values between 0 and 1·76. The bending frequencies of a linear chain are doubly degenerate in the two planes through the axis so that the $n-2$ frequencies (11) represent $2n-4$ vibrations. The $n-1$ valence vibrations are given by the well known formula

$$\nu=\frac{\sin\frac{1}{2}\alpha}{\pi}\sqrt{\frac{f}{m}}, \qquad \alpha=\pi k/n,\ k=1,\ 2,\ \ldots .\ n-1. \qquad \ldots\ldots(12)$$

The $3n-5$ possible vibrations of a linear chain consisting of n mass points are therefore represented by the equations (11) and (12) provided that the particles are subject to valence and angle forces.

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LETTERS TO THE EDITOR

Sessile Dislocations

Let us consider what would at first sight seem to be the simplest sort of dislocation in a close-packed cubic lattice, made, in imagination, by cleaving the crystal part way between two close-packed (i.e. {111}) planes and inserting a close-packed half-plane into the cleft. This can be done with maintenance of close-packing of nearest neighbours for all atoms except those at the edge of the half-plane, i.e. along the dislocation line itself. This would appear to be an ordinary Taylor dislocation (Taylor 1934). However, should this dislocation now glide, in the ordinary manner of a Taylor dislocation, in the direction normal to the added plane, it will bring an ever-increasing number of atoms out of the close-packing arrangement into another arrangement of more open packing and consequently of higher energy : so that this glide is prevented by a large restoring force—so large, we may easily conclude, that the glide would not take place under any macroscopically applicable stress. Such a dislocation will be called " sessile ", in contrast with " glissile " dislocations—those which are capable of glide.

The situation may be clarified by considering the displacement vectors—Burgers vectors (Burgers 1939)—of various possible dislocations. The displacement vector of a perfect dislocation is a lattice vector, $(\frac{1}{2}a,\ \frac{1}{2}a,\ 0)$, with its various permutations, in the close-packed cubic lattice. Besides these perfect dislocations, which transfer atoms from one lattice position to another, there are also imperfect dislocations which transfer atoms from lattice positions to twin-lattice positions. Such are Shockley's " half-dislocations " (Heidenreich and Shockley 1948) with Burgers vector $(a/3,\ a/6,\ a/6)$ which arise by the dissociation of perfect dislocations in a {111} plane, e.g.

$$(\tfrac{1}{2}a,\ -\tfrac{1}{2}a,\ 0)\rightarrow(a/3,\ -a/6,\ -a/6)+(a/6,\ -a/3,\ a/6).$$

Such is also the dislocation with Burgers vector $(a/3,\ a/3,\ a/3)$ described in the first paragraph of this letter, and one with Burgers vector $(-a/3,\ -a/3,\ -a/3)$ obtained by removing instead of adding a close-packed half-plane. Unlike perfect dislocations of opposite sign these two are not equivalent to each other.

Now, atoms in twin-lattice positions only fit correctly on the appropriate composition plane (a {111} plane in these cases) of the main lattice. Hence, whereas a perfect dislocation can glide, without changing the amount of misfit in the crystal, in whatever surface contains the line of the dislocation and its Burgers vector, imperfect dislocations increase the misfit unless they glide in a composition plane. Consequently the only kind of imperfect dislocation which can glide freely is one whose Burgers vector lies in the composition plane of the twin relationship to which it belongs. The imperfect dislocations of $(a/3,\ a/6,\ a/6)$ type, lying in {111} planes, are glissile. The imperfect dislocations $(a/3,\ a/3,\ a/3)$, not lying in {111} planes, and also being incapable of dissociating into glissile partial dislocations, are sessile. The only simple way in which they can move in the lattice is by diffusion processes in which they gain or lose atomic vacancies.

The ways in which these sessile dislocations can be formed (e.g. by the aggregation of vacancies, or by relatively complicated dislocation reactions) will be the subject of a longer communication. It is thought, however, worth while to draw immediate attention to their existence. They have obvious importance in connection with the strength of metals (being fixed sources of stress which exert forces on glissile dislocations) and with crystal growth (Burton, Cabrera and Frank 1949). The sessile Taylor dislocations here described produce the same type of permanent terrace on the {111} faces they intersect as is produced by an (a, 0, 0) screw dislocation in the {100} face of a simple cubic crystal model.

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ABSTRACTS FOR SECTION B

A Photoelectric Type of Acoustic Spectrograph using Sound Film, by D. Brown, C. F. Coleman and J. W. Lyttleton.

ABSTRACT. An account is given of an apparatus which analyses non-recurrent waveforms such as occur in speech, so that frequency-distribution is represented against time in an FT-diagram. From the theory governing such diagrams, no unique representation is possible, the result depending on the analysing convention adopted, but all conventions are governed by the uncertainty relation $\Delta F \Delta T \geqslant 1$. The method employed is an optical one which analyses a continuously moving sound film by means of a frequency-scanning disc, so producing an oscillograph pattern which is photographed on to another moving film. Typical analyses are reproduced and discussed, mainly " speech patterns " which show the composition very clearly. Advantages include the ability to record the amplitude and phase of each component, also the ability to change the analysing convention in any desired manner, for example to give the error-function convention which leads to minimum uncertainty. The paper concludes with considerations of resolving power, spectral line profiles, and amplifier band width requirements.

The Cause of Anisotropy in Permanent Magnet Alloys, by K. Hoselitz and M. McCaig.

ABSTRACT. Measurements of magnetostriction have been made on samples of an anisotropic permanent magnet alloy. From the results it is concluded that the domain magnetization is, in the absence of a field, along that easy crystallographic direction which makes the smallest angle with the axis of anisotropy. This view is supported by measurements of the remanence. The ideal arrangement which obtains after hardening seems to be slightly disturbed during the subsequent tempering operation.

Magnetic Behaviour of Zinc and Cadmium at Low Temperatures, by L. Mackinnon.

ABSTRACT. Following the recent discovery of the de Haas–van Alphen effect in zinc by Marcus at liquid hydrogen temperatures, the effect has been investigated at liquid helium temperatures using (for the most part) a torsion method similar to that used by Shoenberg in investigating bismuth. The effect in zinc takes the form of a variation of the susceptibility along the hexagonal axis which is periodic in the applied magnetic field. An attempt has been made to correlate the results with Landau's explicit formulae and to derive the various relevant parameters (such as effective masses, and degeneracy temperature) for the electrons causing the effect. Only qualitative agreement has been found, so that too much reliance should not be placed on the physical significance of the figures derived; however, it would appear that, as in the case of bismuth, the effect is caused by only a few times 10^{-6} electrons per atom. In spite of its very similar structure, cadmium did not show the effect; it had, however, at liquid helium temperatures, a magnetic anisotropy some six times that at room temperature.

On the Dielectric Properties of a Gas Discharge, by E. E. Salpeter and R. E. B. Makinson.

ABSTRACT. Formal expressions are derived for the space currents and electrode currents produced by a sinusoidal potential difference of angular frequency ω applied between a pair of electrodes at a distance d apart and immersed in a gas discharge. It is shown that the ionized gas behaves like an isotropic medium of dielectric constant $\{1-4\pi ne^2/m\omega^2\}$ and zero conductivity only in the limiting case of $\beta \equiv v/\omega d \ll 1$ where v is the R.M.S. velocity of the free electrons in the gas. The variation of the equivalent dielectric constant and conductivity of the gas with β are sketched. Extensions of Green's reciprocation theorem and of a theorem on induced currents given by W. Shockley are derived in the appendix.

Thermionic Emission from Oxide Coated Cathodes, by D. A. Wright.

ABSTRACT. It is shown experimentally that with Ba/Sr oxide cathodes, the saturated emission depends on the core material in use, and there is some correlation between total coating resistance and saturated pulsed emission. The steady-state D.C. emission is lower than the pulsed emission, but the D.C. emission measured immediately on application of the anode voltage is similar to the pulsed emission. The difference is due to a decay effect with a time constant in the range 1/1,000–1/10 sec., which is similar in many respects to the decay effect studied in an earlier paper on conductivity measurements. It is shown that the application of semiconductor theory can give a consistent account of coating conductivity and emission, provided the concentration of barium in stoichiometric excess is about 3×10^{17} atoms/cm^3. This figure has some experimental support. It is shown that the presence of an interface layer of the type actually detected should cause decay phenomena with a time constant less than 1 μsec. and in most cases less than 1/10 μsec., so that the decay from pulsed to D.C. emission is not due to the capacity effects introduced by the presence of the layer.

With thoria there is little difference thermionically when studied as a coating on tantalum or on tungsten, or as a ceramic tube, and the pulsed emission is about twice the D.C. emission. Experiment and theory indicate that thoria is an excess semiconductor containing a stoichiometric excess of about 10^{18} atoms/cm^3 of thorium. There is very little sensitivity to oxygen, however, at temperatures above 1,850° K.

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